

Spin Dynamics of Radical Pairs in Magnetic Fields



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Abstract

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The remarkable ability of migratory birds to use the geomagnetic field for their navigation has been fascinating scientists for more than 50 years. Extensive studies, from experiments to theories, suggest that avian magnetoreception may arise from photo-induced radical-pair reactions in the birds' eyes. Although the energy for the interaction of a single molecule with a magnetic field as weak as $\sim 50 \mu\text{T}$ is more than a million times smaller than the thermal energy, such weak fields can still significantly influence spin-selective reactions via the modulation of radical-pair spin dynamics.

A navigational cue requires the radical-pair magnetoreceptor to be sensitive to the direction of an external magnetic field. In Chapter 3, I explore the anisotropic weak magnetic field effect on the eigenstructure and the spin dynamics of a model radical pair with respect to the field direction. Then, the feasibility of the "reference-probe" model for radical-pair magnetoreception is studied.

Birds' disorientation in a static magnetic field caused by extremely weak radiofrequency fields is considered to originate in magnetic effects on the sensory molecules, though it is not yet understood exactly in quantitative detail. A more convincing test - reorientation rather than disorientation in a radiofrequency field in the absence of a static magnetic field - is proposed in Chapter 4. Elaborate theoretical study of the resonance effect induced by a radiofrequency field is followed by spin dynamics simulations for flavin-based radical pairs to evaluate the possibility of a "radiofrequency compass".

The " $B_{1/2}$ " value, a parameter that characterises the magnetic field-dependence of the reactions, was found to be larger than expected on the basis of the hyperfine interactions and to have significant time-dependence. This behaviour is considered as a strong indication of spin relaxation. In Chapter 5, I present several possible candidate spin relaxation mechanisms and find the specific one, singlet-triplet dephasing (STD), that could account for the time-dependent magnetic field effect. In cryptochromes, the only candidate magnetoreceptor, STD probably originates in the electron hopping between tryptophans. Furthermore, simulation shows that STD, even quicker than chemical reactions, does not seem to destroy the directional sensitivity of the FAD-Trp radical pair to weak magnetic fields.

Chiral molecules could act as spin filters that preferentially transmit electrons with spins polarized parallel or antiparallel to their direction of motion. This chiral-induced spin selectivity (CISS), as a spin polarization effect that could be observable by electron paramagnetic resonance (EPR) experiments, is included in the radical pair mechanism in Chapter 6. CISS effects offer the possibility of evolving a more sensitive or precise compass. The associated lack of field-inversion symmetry potentially explains the observation of a polar magnetic compass response.

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Chapter 1

Introduction

Migratory songbirds possess such remarkably proficient navigation ability as to travel vast distances, up to 25000 km [1–5], between wintering and breeding grounds each year with exceptional precision [6]. Among various directional cues, such as the sun [7–9], the stars [10–12] and landmarks en route [6, 13], the Earth’s magnetic field offers crucially useful directional information for birds, especially over large distances [1, 14–16]. Although the magnetic sense of avian species, along with other animals such as cockroaches [17], wood mice [18, 19] and sea turtles [20], has been extensively studied for more than 50 years, the underlying biophysical mechanism is still a mystery and remains one of the most significant unsolved problems in sensory biology.

Apart from directly tracking free-flying birds using radio transmitters for insights into their migratory routes and flight behaviour [1], the avian magnetic compass has been intensively studied by testing birds’ orientation under an artificially controlled magnetic field in a set-up called an “Emlen funnel” [21]. No directional cue other than the external magnetic field generated by a coil system is given in the funnel. Birds’ attempt to escape the funnel in their preferred migratory direction, known as migratory restlessness [22], is demonstrated by the scratches they left on the scratch-sensitive papers placed in the funnel. Statistical

analysis based on these scratch papers determines the birds' orientation as a result of the application of the magnetic field. The birds would randomly orient if the external magnetic field did not participate in their migratory restlessness. Such behavioural experiments, in which birds reoriented when the direction of the external magnetic field is rotated, have established the existence of the avian magnetic compass sense [15, 23]. Significantly, birds' detection of the magnetic field direction relies on the inclination rather than the polarity of the field [15, 24], i.e. inverting the magnetic field maintains the same preferred orientation. This "inclination" compass is interpreted, in the context of avian navigation, as birds' ability to sense the angle between the geomagnetic field axis and the horizontal instead of the magnetic polarity - the information source of a magnetite compass, e.g. the man-made compass needle. However, the sense of the magnetic inclination does not seem universal in animal magnetoreception. Reports of a polarity compass of other animals, such as honeybees [25] and lobsters [26], suggest that more than one mechanism may participate in the process of sensing the geomagnetic field.

The leading hypothesis for geomagnetic sensing involves magnetically sensitive chemical intermediates known as radical¹ pairs [27, 28]. This mechanism is consistent with birds' sense of magnetic inclination, and thereby seems to form the basis of avian magnetoreception. The competing hypothesis, known as the magnetite mechanism, is based on the response of magnetic iron-containing nanoparticles to the external magnetic field [29–31]. This mechanism is unlikely to be responsible for birds' magnetic-compass orientation, though it is potentially involved in birds' detecting magnetic-map information, i.e. the ability to locate their positions on Earth using local geomagnetic information [32, 33].

¹A radical is an atom, molecule, or ion that has at least one unpaired valence electron, normally formed through the homolysis of weak bonds or electron transfer.

Furthermore, behavioural experiments suggest that the biological magnetic compass of animals, such as birds [34–37], newts [38] and beetles [39], is light-dependent. Light-dependence is apparently not a property belonging to the magnetite mechanism, but coincides with the photochemical transformation with a radical pair as a transient reaction intermediate in the radical pair mechanism. Moreover, the light-dependent compass is wavelength-dependent [36, 37]: birds tend to orient well under light in the wavelength range 400–565 nm, but they orient randomly if they are kept under red light or completely in the darkness. Such photo-induced magnetic sensor is most likely to be located in the eyes, though the magnetic sensitive radical-pair reactions possibly occur, in principle, almost anywhere in a bird’s body considering of the transparency of biological tissue to static and low-frequency magnetic fields and the absence of any obvious magnetosensory organ.

Experimental and computational studies [40–45] suggest that radiofrequency (RF) fields could remarkably influence radical pair reactions via the RF-induced resonance between energy levels of the magnetic interactions in a radical pair. Behavioural experiments [46–49] in which birds exposed to weak RF fields lose their ability to orient in the geomagnetic field provide arguably the strongest evidence for the radical pair mechanism, though the exact RF conditions needed to disrupt the compass still stay undetermined. In 2009, Ritz *et al.* reported that an extremely weak (15 nT) RF field at the Larmor frequency of a free electron in the local geomagnetic field was sufficient to prevent birds from using their magnetic compass, suggesting that the unpaired electron in one of the radicals must be isolated from any magnetic interaction within the radical pair [48]. However, this discovery was challenged by a recent study [49] with the aim to replicate the experiments of Ritz *et al.*. Although failing to see specific effects on the birds’

magnetic compass orientation capabilities using fields at the Larmor frequency, this study found that weak, broadband RF noise causes significant disorientation of birds.

1.1 Radical pair mechanism

Until the 1970s [50, 51], magnetic fields had not been realised to alter the rate or yield of a chemical reaction by most scientists, due to the far smaller² energy associated with the magnetic interactions of typical molecules than the thermal energy, $k_B T$ with k_B Boltzmann constant and T temperature, which is associated with the random molecular motions - rotation and vibration. Note that in thermal equilibrium, energies required to alter the rate or yield of a chemical transformation should be at least comparable to the energy associated with these motions. However, a system at the state far from equilibrium indeed allows delicate interactions to have significant effects. In the context of magnetic sensitive reactions, the non-equilibrium state is the spin-correlated radical pair.

A radical pair consists of two radicals created simultaneously usually by a chemical reaction such as homolytic bond-breaking (e.g. $\text{CH}_4 \rightarrow [\text{CH}_3^\bullet \text{ H}^\bullet]$ where “ $\bullet$ ” denotes the unpaired electron and $[\dots]$ indicates the radical pair). Radical pairs, formed through electron transfer (ET) and able to recombine according to their spin states, were first proposed by Schulten *et al.* in 1978 to account for the avian magnetic-compass sense [28]. A simple model [52] for the ET-induced radical pair comprises an electron donor, D, and acceptor, A. Photo-excitation of A causes the electron to be passed from the closed shell D to A^* (“ $*$ ” denotes the photo-excited state), $D + A^* \rightarrow [D^{\bullet+} A^{\bullet-}]$. In many organic radicals, the lack of

²The interaction of the geomagnetic magnetic field (30-65 μT) with a single molecule is more than a million times smaller than its thermal energy under physiological conditions.

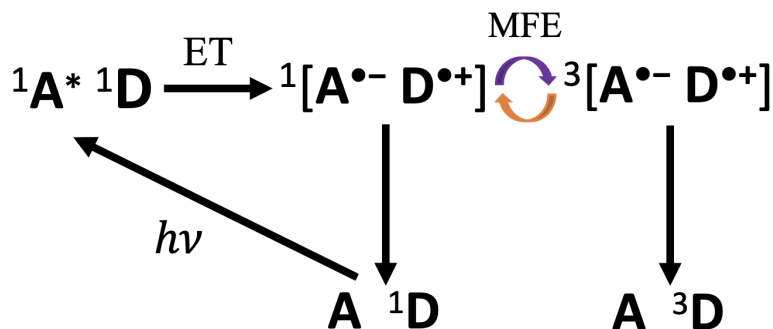


Figure 1.1: Reaction scheme for a simple radical-pair model.

heavy atoms (e.g. transitional metal) causes tiny spin-orbit couplings and low symmetry leads to quenching of orbital angular momentum. Thus, the exchange of spin and orbital angular momentum is inefficient and can appropriately be ignored in the process of electron transfer. Hence, spin angular momentum is conserved in the formation of a radical pair. Assume that ET is immediately followed by the photo-excitation before any appreciable inter-system crossing can happen, so that the radical pair $[\mathbf{D}^{\bullet+} \mathbf{A}^{\bullet-}]$ is generated in a (spin) singlet state (Figure 1.1), i.e. the two unpaired electron spins are arranged anti-parallel to each other. Conventionally, the conservation of electron spin is considered as a fundamental requirement for radical-pair based magnetoreception. However, this could be changed by the consideration of the chirality of the medium the electron travels through (detailed discussion in Chapter 6).

The singlet state is also non-stationary because the two unpaired electrons are coupled to different nuclei in each radical where they are respectively localized. Therefore, the radical-pair spin state, driven by magnetic interactions, will evolve over time, and the time evolution is represented by the coherent interconversion between the electronic singlet and triplet states. Usually, among these magnetic interactions within a radical pair, the hyperfine interactions of the electron spins with the nuclear spins show the greatest significance in the singlet-triplet

interconversion. Even as weak as the geomagnetic field of 50 μT , an external magnetic field can remarkably modulate the singlet-triplet interconversion via the Zeeman interaction with the unpaired electrons. Significantly, this modulation of the radical-pair spin dynamics is anisotropic with respect to the direction of the magnetic field, as a result of the anisotropic hyperfine interactions in the radicals (detailed discussion in Chapter 3). This directional dependence of the singlet-triplet interconversion on the external magnetic field forms the basis of the radical-pair compass. Hence, radical pairs in the magnetoreceptor must align in a specific order to preserve the anisotropy of the hyperfine interactions in a radical pair from being averaged out over all the pairs. Inter-radical spin interactions, on the other hand, cause extra energy gaps between the singlet and triplet states, which generally hinder the singlet-triplet interconversion. Thus, a sensitive magnetoreceptor cannot rely on radical pairs with inter-radical interactions much stronger than the hyperfine interactions.

The spin-selective recombination of a radical pair, i.e. the back electron transfer to obtain either the singlet or the triplet product (Figure 1.1): ${}^{1(3)}[\text{D}^{\bullet+} \text{A}^{\bullet-}] \rightarrow {}^{1(3)}\text{D} + \text{A}$ where “1” and “3” denote singlet and triplet respectively, depends not only on the two reaction rate constants but also on the extent and frequency of the singlet-triplet interconversion [28]. Besides, reactions could involve only one of the radicals and form a product from both the singlet and triplet fractions of the radical pair [53]. Although spin-independent, such reaction provides a competing pathway for the radical-pair recombination. The magnetic field effect on the spin dynamics is captured in the yields of the radical pair reactions. The core assumption of the radical pair mechanism in avian magnetoreception is that the navigation information for birds’ migration encodes in the field-modulated yields of the radical pair reactions. In 1998, Timmel *et al.* found that weak

magnetic fields promote the efficiency of the singlet-triplet interconversion through breaking the degeneracy of the energy levels of the magnetic interactions in a radical pair [54], so that the triplet product benefits from the external magnetic field with a corresponding decrease in the singlet product for a singlet-born radical pair. Computational study [55] shows that the reaction yield of a radical pair with anisotropic hyperfine interactions is indeed closely related to the direction of the external weak magnetic field $\sim 50 \mu\text{T}$. In 2016, Hiscock *et al.* proposed that the high angular precision of the radical pair compass may originate in a “quantum needle” arising from the avoided crossings of the quantum mechanical spin energy-levels of radicals [56]. Recently, Kattnig *et al.* predicted that the directional sensitivity of a radical-pair magnetic compass could be significantly enhanced by the “scavenging” reaction of one of the radicals with an external paramagnetic molecule [57]. All these studies make it promising for the radical pair mechanism to account for the avian magnetoreception, though the concrete comprehensive description of the actual radical-pair magnetic sensor for avian migration is still unknown. The major difficulty comes from the serious challenge of experimental detection of the anisotropic weak ($\sim 50 \mu\text{T}$) magnetic field effects on the proposed magnetoreceptors.

A sensitive radical-pair compass requires that the radical pair remains in a coherent spin state for a lifetime as long as at least one Larmor period, $T_L = 1/\nu_L$. For a $50 \mu\text{T}$ magnetic field, $T_L \approx 700 \text{ ns}$. However, various stochastic modulations of local magnetic fields, induced by unavoidable thermal motions, inevitably relax the coherent spin state to equilibrium. Generally, spin relaxation, much quicker than 700 ns , is considered to wipe out the coherent oscillations in spin dynamics (Figure 1.1) before a magnetic field $\sim 50 \mu\text{T}$ could show any noticeable effect on the singlet-triplet interconversion. Unfortunately, there still lacks an accurate

description of the actual relaxation mechanisms in radical-pair magnetoreception [58–62], though studies [63, 64] with consideration of the stochastic modulation of hyperfine interactions show that spin relaxation may not completely remove the compass property of the proposed radical-pair magnetoreceptor. Moreover, certain spin relaxation mechanism could enhance the directional sensitivity of a radical-pair compass [65]. In Chapter 5, we will show that this spin relaxation, even faster than the chemical reactions, probably participates in the magnetic sensing and could account for the time-dependent magnetic field effect.

1.2 Cryptochrome

In 2000, Schulten *et al.* proposed that cryptochromes, in the same family of proteins as photolyases [66–69], might be the photo-induced magnetoreceptor to form radical pairs, sensitive to magnetic fields, for avian navigation. Even to this day, this protein remains the only candidate radical-pair magnetoreceptor [70–72]. However, concrete evidence that cryptochromes actually account for the birds’ compass orientation is still lacking, though various reports [71, 73–77] suggest that cryptochromes are involved in animal magnetic-field-dependent behaviours - their effects could merely be embodied in the signalling pathway.

An equivocal evidence is that some cryptochromes contain a redox-active flavin adenine dinucleotide co-factor (FAD), a chromophore with an absorption band covering 400–500 nm approximately matching the photo-activation wavelength of the avian magnetic compass [36, 37, 78]. The photo-excitation of FAD is followed by sequential electron transfers along the conserved tryptophan (Trp) residues (Figure 1.2) [79], so that a singlet radical pair, consisting of the flavosemiquinone radical ($\text{FAD}^{\bullet-}$) and the terminal tryptophan radical ($\text{TrpH}^{\bullet+}$), is formed. The evolution of the spin state of the $[\text{FAD}^{\bullet-} \text{TrpH}^{\bullet+}]$ radical pair, RP1, mainly

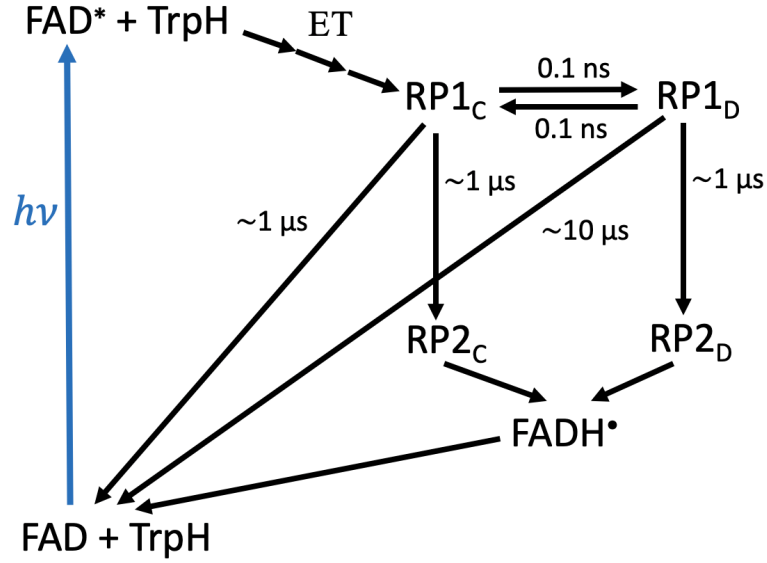


Figure 1.2: Scheme for the radical-pair reactions in Cry4. Photo-excitation (blue light) of FAD is followed by sequential electron transfers to form the long-lived ($\sim 1 \mu\text{s}$) radical pairs. $\text{RP1}_{C(D)}$ denotes the $[\text{FAD}^{\bullet-} \text{Trp}_{C(D)}\text{H}^{\bullet+}]$ radical pair. $\text{RP2}_{C(D)}$ denotes the $[\text{FAD}^{\bullet-} \text{Trp}^{\bullet}_{C(D)}]$ radical pair. Fast electron hopping ($\sim 0.1 \text{ ns}$) between RP1_C and RP1_D gives rise to a composite radical pair which is thought to account for the magnetic sensing process. RP2_C and RP2_D are stabilized radical pairs that on a long timescale ($> 1 \text{ ms}$) give the $\text{FADH}^\bullet$ radical state, as the potential signalling state.

originates from various hyperfine interactions (see Appendix A) and is modulated by external magnetic fields. Reverse electron transfer allows the radical pair to return to the reactant state. In cryptochromes, only the singlet radical pair, $^1[\text{FAD}^{\bullet-} \text{TrpH}^{\bullet+}]$, can possibly recombine to the ground state, $\text{FAD} + \text{TrpH}$, i.e. there is no accessible triplet product state of cryptochrome that could be formed spin-selectively from the triplet radical pair [53, 79, 80]. The spin-independent deprotonation of the $\text{TrpH}^{\bullet+}$ radical gives a secondary radical pair, $[\text{FAD}^{\bullet-} \text{Trp}^\bullet]$ RP2 , with the spin correlation inherited from the $[\text{FAD}^{\bullet-} \text{TrpH}^{\bullet+}]$ radical pair. Both reaction pathways occur on a time-scale of $1 \mu\text{s}$ [79], which satisfies the condition for a weak magnetic field $\sim 50 \mu\text{T}$ to appreciably modulate the yields of the products. $[\text{FAD}^{\bullet-} \text{Trp}^\bullet]$ radical pair has a lifetime more than 1 ms , such a long time-scale that the coherent spin state would be well relaxed before the spin-selective recombination could proceed to a significant extent. Thus, no

magnetic field effect is expected from the spin dynamics of the $[\text{FAD}^{\bullet-} \text{Trp}^{\bullet}]$ radical pair. Furthermore, protonation of the $\text{FAD}^{\bullet-}$ radical, giving the stabilized $\text{FADH}^{\bullet}$, takes a longer time (e.g. > 1 ms in robin cryptochrome 4a [79]). $\text{FADH}^{\bullet}$ is supposed to have the function of triggering the biochemical signalling cascade [53, 79].

Six cryptochromes (Cry1a, Cry1b, Cry2a, Cry2b, Cry4a and Cry4b), found in birds' retina cells, were expected to account for the light-dependent magnetoreceptor [71, 73, 75, 81, 82]. However, studies [83] suggest that avian Cry1a and Cry2 proteins may not bind FAD strongly *in vitro*, as the key amino acid residues used to bind FAD in *DmCry* (fly *Drosophila melanogaster*) may be missing. A recent photochemistry study [79] shows that Cry4 from the night-migratory European robin (*Erithacus rubecula*), with good flavin binding, is magnetically sensitive *in vitro*. In the same study, greater magnetic-field-induced change in the yield of the reaction product for *ErCry4* has been detected than that for *GgCry4* (chicken *Gallus gallus*) and for *ClCry4* (pigeon *Columba livia*), two non-migratory bird species. Electron transfer involving a tetrad of tryptophans in Cry4 gives the FAD-Trp_D radical pair with lifetime $\sim 10 \mu\text{s}$. Although the FAD-Trp_C radical pair seems to be responsible for the major magnetic sensing process [79], the rapid electron hopping between Trp_C and Trp_D gives rise to a composite radical pair, which was shown by a recent computational study [84] to have potentially better directional sensitivity to weak magnetic fields than the FAD-Trp_C radical pair.

Chapter 2

Theories and fundamentals

Spin dynamics is essential for radical pair based magnetoreception. This chapter is concerned with the basic concepts related to spin dynamics, how a weak magnetic field can potentially affect the spin dynamics, how this effect can be quantitatively described, and how spin relaxation is included in the spin dynamics simulation.

2.1 Rotation and angular momentum

In quantum mechanics, the position and momentum of a particle are characterized by (vector) operators, $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$. The momentum operator $\hat{\mathbf{p}}$ is the generator of an infinitesimal translation operator, $\hat{\mathcal{T}}_{(\mathbf{dx})} = 1 - i\hat{\mathbf{p}} \cdot \mathbf{dx}/\hbar$ [85]. $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ have the commutation relation:

$$[\hat{x}_k, \hat{p}_j] = i\hbar\delta_{kj} \text{ for all } k, j \in \{x, y, z\}, \quad (2.1)$$

where $\hbar$ is the reduced Planck constant, $[A, B] = AB - BA$, and $\hat{x}_k$ and $\hat{p}_j$ denote the component operators of $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$. The orbital angular momentum operator $\hat{\mathbf{L}}$ is defined as the cross product of $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$,

$$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}}. \quad (2.2)$$

Thus, the commutation relation among the component operators of $\hat{\mathbf{L}}$ (i.e. $\hat{L}_x = \hat{x}_y \hat{p}_z - \hat{x}_z \hat{p}_y$, $\hat{L}_y = \hat{x}_z \hat{p}_x - \hat{x}_x \hat{p}_z$ and $\hat{L}_z = \hat{x}_x \hat{p}_y - \hat{x}_y \hat{p}_x$) can be obtained according

2.1. Rotation and angular momentum

to the commutation relation in equation (2.1) [86]:

$$[\hat{L}_i, \hat{L}_j] = i\epsilon_{ijk}\hbar\hat{L}_k \quad \text{for all } i, j, k \in \{x, y, z\}, \quad (2.3)$$

where ϵ_{ijk} denotes the Levi-Civita symbol with $\epsilon_{xyz} = 1$. The orbital angular momentum is quantized, and the eigenvalues of $\hat{L}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}}$ are $l(l+1)\hbar^2$ where $l = 0, 1, 2, \dots$ is the orbital quantum number [86].

2.1.1 Spin angular momentum

In quantum mechanics, the angular momentum can possibly be irrelevant to the position and the linear momentum of a particle, because of the existence of spin angular momentum (or simply spin). Spin is an intrinsic form of angular momentum carried by elementary particles, and thus by some atomic nuclei. It was inferred by experiments, such as the Stern-Gerlach experiment, where the quantized magnetic moment of the electron $\boldsymbol{\mu}_e$ was discovered. This magnetic moment was later realized to be attributed to the quantized spin angular momentum characterized by the spin vector operator $\hat{\mathbf{S}}$. This magnetic moment $\boldsymbol{\mu}_e$ is:

$$\boldsymbol{\mu}_e = -g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}}, \quad (2.4)$$

where $g_e \simeq 2.0023$ is the Landé spin g -factor for a free electron, which was predicted and calculated using the Dirac equation, a relativistic wave equation, $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton where m_e is the mass of an electron and e is the elementary positive charge. The minus sign in equation (2.4) results from the negative electric charge carried by a single electron. $\boldsymbol{\mu}_e$ can alternatively be written as:

$$\boldsymbol{\mu}_e = \gamma_e \hat{\mathbf{S}}, \quad (2.5)$$

where $\gamma_e \simeq -1.7609 \times 10^{11} \text{ rad} \cdot \text{s}^{-1} \cdot \text{T}^{-1}$ is the gyromagnetic ratio for an electron.

Although the spin angular momentum is not related to $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$, it is defined as the generator of an infinitesimal rotation operator of the spin state ket in Hilbert space [85]. Before giving the detailed introduction of the rotation operator, we first look at an infinitesimal rotation of any three-dimensional vector denoted by $R_{(\mathbf{n}, \delta\phi)}$, where $\mathbf{n}$ as a unit vector represents the rotation axis, and $\delta\phi$ denotes a small angle. $R_{(\mathbf{n}, \delta\phi)}$ is described by the SO(3) group (the special orthogonal group in three dimensions), which contains three basis generators (in physics convention):

$$R_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, R_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, R_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2.6)$$

Then, $R_{(\mathbf{n}, \delta\phi)}$ can be expressed as:

$$R_{(\mathbf{n}, \delta\phi)} = 1 - i(\mathbf{R} \cdot \mathbf{n})\delta\phi, \quad (2.7)$$

where $\mathbf{R}$ denotes the vector with R_x , R_y and R_z as its three components. A finite rotation around $\mathbf{n}$ is obtained by compounding successive infinitesimal rotations:

$$R_{(\mathbf{n}, \phi)} = \lim_{N \rightarrow \infty} (1 - i(\mathbf{R} \cdot \mathbf{n})\frac{\phi}{N})^N = e^{-i(\mathbf{R} \cdot \mathbf{n})\phi}. \quad (2.8)$$

Then, the rotation of the vector spin operator $\hat{\mathbf{S}}$, around the z -axis for instance, is:

$$\begin{aligned} \hat{\mathbf{S}}' &= R_{(\mathbf{z}, \phi)}\hat{\mathbf{S}} = e^{-iR_z\phi}\hat{\mathbf{S}} \\ &= \begin{pmatrix} \cos(\phi) & -\sin(\phi) & 0 \\ \sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix} \\ &= \begin{pmatrix} \cos(\phi)\hat{S}_x - \sin(\phi)\hat{S}_y \\ \sin(\phi)\hat{S}_x + \cos(\phi)\hat{S}_y \\ \hat{S}_z \end{pmatrix}. \end{aligned} \quad (2.9)$$

Note that the rotation generators in equation (2.6) do not commute with each other, and they have the commutation relation:

$$[R_i, R_j] = i\epsilon_{ijk}R_k \quad \text{for all } i, k, j \in \{x, y, z\}, \quad (2.10)$$

2.1. Rotation and angular momentum

that is same with the commutation relation in equation (2.3) when taking $\hbar$ as unity. This verifies the general definition of the angular momentum in quantum mechanics as the generator of a rotation in Hilbert space.

The infinitesimal rotation of a spin state ket is written as $\mathcal{D}_{(\mathbf{n}, \delta\phi)}$ which is described in the SU(2) group (the special unitary group in two dimensions). For a spin-1/2 particle such as the electron, the three component spin operators are:

$$\hat{S}_x = \frac{1}{2}\sigma_x, \hat{S}_y = \frac{1}{2}\sigma_y, \hat{S}_z = \frac{1}{2}\sigma_z, \quad (2.11)$$

where σ_k denotes the Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.12)$$

Note that we set $\hbar = 1$ throughout the rest of this thesis. Then, the representation of $\mathcal{D}_{(\mathbf{n}, \delta\phi)}$ is given:

$$\mathcal{D}_{(\mathbf{n}, \delta\phi)} = 1 - i(\hat{\mathbf{S}} \cdot \mathbf{n})\delta\phi. \quad (2.13)$$

In analogy with equation (2.8), a finite rotation for the spin state ket is obtained:

$$\mathcal{D}_{(\mathbf{n}, \phi)} = e^{-i(\hat{\mathbf{S}} \cdot \mathbf{n})\phi}. \quad (2.14)$$

Then, a spin state ket $|\alpha\rangle$ after a finite rotation is:

$$|\alpha'\rangle = \mathcal{D}_{(\mathbf{n}, \phi)}|\alpha\rangle. \quad (2.15)$$

As a result of such rotation, the expectation value of the spin angular momentum becomes:

$$\langle\alpha'|\hat{S}_j|\alpha'\rangle = \langle\alpha|\mathcal{D}_{(\mathbf{n}, \phi)}^\dagger \hat{S}_j \mathcal{D}_{(\mathbf{n}, \phi)}|\alpha\rangle \quad \text{for all } j \in \{x, y, z\}. \quad (2.16)$$

This is equivalent to applying a rotation operation to the component spin operators instead of the state ket:

$$\hat{S}'_j = \mathcal{D}_{(\mathbf{n}, \phi)}^\dagger \hat{S}_j \mathcal{D}_{(\mathbf{n}, \phi)}. \quad (2.17)$$

Such rotation to $\hat{S}_j$ is equal to $R_{(\mathbf{n}, \phi)}$ acting on the vector spin operator $\hat{\mathbf{S}}$ [85]:

$$\mathcal{D}_{(\mathbf{n}, \phi)}^\dagger \hat{S}_j \mathcal{D}_{(\mathbf{n}, \phi)} = \sum_{k=x, y, z} R_{(\mathbf{n}, \phi)jk} \hat{S}_k \quad \text{for all } j \in \{x, y, z\}, \quad (2.18)$$

where $R_{(\mathbf{n}, \phi)}$ is viewed as a matrix and $R_{(\mathbf{n}, \phi)jk}$ denotes a matrix element. This can be verified by the example of a rotation of the component spin operators around the z -axis:

$$\begin{aligned} \mathcal{D}_{(z, \phi)}^\dagger \hat{S}_x \mathcal{D}_{(z, \phi)} &= e^{i\hat{S}_z \phi} \hat{S}_x e^{-i\hat{S}_z \phi} = \begin{pmatrix} 0 & \frac{1}{2}e^{i\phi} \\ \frac{1}{2}e^{-i\phi} & 0 \end{pmatrix} = \cos(\phi) \hat{S}_x - \sin(\phi) \hat{S}_y, \\ \mathcal{D}_{(z, \phi)}^\dagger \hat{S}_y \mathcal{D}_{(z, \phi)} &= e^{i\hat{S}_z \phi} \hat{S}_y e^{-i\hat{S}_z \phi} = \begin{pmatrix} 0 & -\frac{i}{2}e^{i\phi} \\ \frac{i}{2}e^{-i\phi} & 0 \end{pmatrix} = \sin(\phi) \hat{S}_x + \cos(\phi) \hat{S}_y, \\ \mathcal{D}_{(z, \phi)}^\dagger \hat{S}_z \mathcal{D}_{(z, \phi)} &= e^{i\hat{S}_z \phi} \hat{S}_z e^{-i\hat{S}_z \phi} = \hat{S}_z, \end{aligned} \quad (2.19)$$

which coincides with equation (2.9).

2.1.2 Higher spin

Apart from electrons, atomic nuclei can have spin angular momentum. As a nucleus is composed of protons and neutrons (both of which are spin-1/2 particles), the spin quantum number of a nucleus can either be integer or half-integer. For instance, the ^1H nucleus (a proton) has a spin quantum number $s = 1/2$, ^{14}N has $s = 1$, and ^{17}O has $s = 5/2$. Although the spin quantum number of atomic nuclei can be higher than that of the electron, the fundamental commutation relation among the component spin operators is invariant:

$$[\hat{S}_i, \hat{S}_j] = i\epsilon_{ijk} \hat{S}_k \quad \text{for all } i, j, k \in \{x, y, z\}. \quad (2.20)$$

Note that all of the component spin operators commute with the operator which characterizes the total spin angular momentum, $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$. Therefore, $\hat{S}_j$ and $\hat{S}^2$ share the same set of eigenstates:

$$\begin{aligned} \hat{S}^2 |s, m_s\rangle &= s(s+1) |s, m_s\rangle, \\ \hat{S}_z |s, m_s\rangle &= m_s |s, m_s\rangle \quad \text{with } m_s \in \{-s, -s+1, \dots, s-1, s\}, \end{aligned} \quad (2.21)$$

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where m_s is the so-called spin projection quantum number ranging from $-s$ to s with a step of 1. Note that here we follow the convention that $\hat{S}_z$ is diagonal. Thus, there exist a “ladder” of $2s + 1$ eigenvalues for $\hat{S}_z$, and this “ladder” is described by two operators $\hat{S}_\pm$ (where $+$ and $-$ respectively mean step up and down). $\hat{S}_\pm$ are defined as:

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y. \quad (2.22)$$

From this definition and the commutation relation in equation (2.20), one will find that the two ladder operators satisfy the commutation relations:

$$[\hat{S}_+, \hat{S}_-] = 2\hat{S}_z, [\hat{S}_z, \hat{S}_\pm] = \pm\hat{S}_\pm. \quad (2.23)$$

Based on such commutation relations, the action of $\hat{S}_\pm$ on the eigenstates of $\hat{S}_z$ gives [85]:

$$\hat{S}_\pm |s, m_s\rangle = \sqrt{(s \mp m_s)(s \pm m_s + 1)} |s, m_s \pm 1\rangle. \quad (2.24)$$

Note that this is not restricted to the spin-1/2 particle. Higher spin angular momentum operators are thus obtained with the diagonal $\hat{S}_z$, and $\hat{S}_x$ and $\hat{S}_y$ expressed by $\hat{S}_\pm$:

$$\hat{S}_x = \frac{\hat{S}_+ + \hat{S}_-}{2}, \quad \hat{S}_y = \frac{\hat{S}_+ - \hat{S}_-}{2i}. \quad (2.25)$$

Taking the spin-1 particle (such as ^{14}N) as an example, m_s is allowed to be 1, 0 or -1 , the three diagonal elements of $\hat{S}_z$. Matrix elements of $\hat{S}_x$ and $\hat{S}_y$ in the eigenbasis of $\hat{S}_z$ are obtained by equations (2.24) and (2.25). Then, the representations of the three component spin operators are:

$$\hat{S}_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \hat{S}_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}. \quad (2.26)$$

2.1.3 The 2π rotation

The equivalence between the two ways of rotation either for the component spin operators, $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$, in Hilbert space or for the vector spin operator, $\hat{\mathbf{S}}$, in the

three-dimensional real space is demonstrated by equation (2.18). This equivalence originates from the same commutation relation of the generators of the SU(2) group and the SO(3) group. However, the inference that there is a one-to-one correspondence between the two groups is incorrect [85]. A rotation of 2π described by the SO(3) group language makes no difference to the three-dimensional vector (i.e. the rotation matrix is an identity matrix, $R_{(\mathbf{n}, 2\pi)} = \hat{\mathbb{1}}$). Whereas such 2π rotation in the SU(2) group language is not necessarily represented by the identity matrix for a spin state ket.

A state $|\alpha\rangle$ of spin- s can be expanded in the eigenbasis of $\hat{S}_z$:

$$|\alpha\rangle = \sum_{m_s} c_{s, m_s}^{\alpha} |s, m_s\rangle, \quad (2.27)$$

where $c_{s, m_s}^{\alpha} = \langle s, m_s | \alpha \rangle$. A 2π rotation around the z -axis gives $|\alpha'\rangle$,

$$|\alpha'\rangle = \mathcal{D}_{(\mathbf{z}, 2\pi)} |\alpha\rangle = e^{-i\hat{S}_z 2\pi} \sum_{m_s} c_{s, m_s}^{\alpha} |s, m_s\rangle = \sum_{m_s} e^{-i2m_s\pi} c_{s, m_s}^{\alpha} |s, m_s\rangle. \quad (2.28)$$

The phase of every $|s, m_s\rangle$ element becomes $e^{-i2m_s\pi}$. If s is a half-integer, so is m_s . Thus, $e^{-i2m_s\pi} = -1$, regardless of which m_s it is. Similarly, if s is an integer, so is m_s and $e^{-i2m_s\pi} = 1$. Then, $\mathcal{D}_{(\mathbf{z}, 2\pi)}$ can be represented in terms of s :

$$\mathcal{D}_{(\mathbf{z}, 2\pi)} = (-1)^{2s} \hat{\mathbb{1}}. \quad (2.29)$$

This can be generalized to an arbitrary rotation axis characterized by a unit vector, $\mathbf{n} = (n_x, n_y, n_z)^{\mathsf{T}}$, where the superscript “ T ” denotes the transpose. $\mathbf{n}$ can be viewed as $\mathbf{z} = (0, 0, 1)^{\mathsf{T}}$ after a rotation denoted by R_{ra} :

$$\mathbf{n} = R_{\text{ra}} \mathbf{z}. \quad (2.30)$$

Remembering the representation for $\mathcal{D}_{(\mathbf{n}, \phi)}$ in equation (2.14), $\hat{\mathbf{S}} \cdot \mathbf{n}$ now is:

$$\hat{\mathbf{S}} \cdot \mathbf{n} = \hat{\mathbf{S}}^{\mathsf{T}} \mathbf{n} = \hat{\mathbf{S}}^{\mathsf{T}} (R_{\text{ra}} \mathbf{z}) = (R_{\text{ra}}^{\mathsf{T}} \hat{\mathbf{S}})^{\mathsf{T}} \mathbf{z} = (R_{\text{ra}}^{-1} \hat{\mathbf{S}})^{\mathsf{T}} \mathbf{z}, \quad (2.31)$$

2.2. Addition of spin

where $R^\top = R^{-1}$ meaning a reverse rotation in the $\text{SO}(3)$ group has been used. Here, the rotation of $\mathbf{z}$ has been transformed to a reverse rotation of the vector spin operator $\hat{\mathbf{S}}$. Using equation (2.18) and noting that any rotation operator $\mathcal{D}$ is unitary, the component spin operators after such reverse rotation are obtained:

$$\hat{S}'_j = \sum_{k=x,y,z} (R_{\text{ra}}^{-1})_{jk} \hat{S}_k = \mathcal{D}_{\text{ra}} \hat{S}_j \mathcal{D}_{\text{ra}}^\dagger. \quad (2.32)$$

Then, $\hat{\mathbf{S}} \cdot \mathbf{n}$ in equation (2.31) becomes $\hat{S}'_z = \mathcal{D}_{\text{ra}} \hat{S}_z \mathcal{D}_{\text{ra}}^\dagger$. Therefore, $\mathcal{D}_{(\mathbf{n}, 2\pi)}$ is obtained:

$$\mathcal{D}_{(\mathbf{n}, 2\pi)} = e^{-i\mathcal{D}_{\text{ra}} \hat{S}_z \mathcal{D}_{\text{ra}}^\dagger 2\pi} = \mathcal{D}_{\text{ra}} e^{-i\hat{S}_z 2\pi} \mathcal{D}_{\text{ra}}^\dagger = \mathcal{D}_{\text{ra}} \mathcal{D}_{(\mathbf{z}, 2\pi)} \mathcal{D}_{\text{ra}}^\dagger. \quad (2.33)$$

Recalling $\mathcal{D}_{(\mathbf{z}, 2\pi)}$ in equation (2.29), we have:

$$\mathcal{D}_{(\mathbf{n}, 2\pi)} = (-1)^{2s} \hat{\mathbb{1}}. \quad (2.34)$$

In conclusion, for an integer spin, the 2π rotation will return the state ket, whereas for a half-integer spin, the state ket will differ from the original ket by a minus sign after the 2π rotation. This is the fundamental basis of the Kramers degeneracy which will be discussed in detail in Chapter 4 about the effect of a resonant radiofrequency field on a radical pair.

2.2 Addition of spin

The spin-selective reactions of organic radical pairs generally involve multiple spins – mainly the two unpaired electrons and the nuclear spins, among which there exist spin interactions that are responsible for the time evolution of the radical pair spin state. To describe the states of the combined spins, we need the tensor product operation “ $\otimes$ ” which stands for a product between elements of different Hilbert spaces denoted by $\mathcal{H}$. The tensor product forms a larger Hilbert space, taking two matrices A and B (suppose they are both 2×2 matrices) respectively

in $\mathcal{H}^A$ and $\mathcal{H}^B$ for example,

$$A \otimes B = \begin{pmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{pmatrix}. \quad (2.35)$$

The tensor product has a significant property:

$$(AD) \otimes (CB) = (A \otimes C)(D \otimes B). \quad (2.36)$$

Thus, $A \otimes B$ is re-written as:

$$A \otimes B = (A \mathbb{1}^A) \otimes (\mathbb{1}^B B) = (A \otimes \mathbb{1}^B)(\mathbb{1}^A \otimes B), \quad (2.37)$$

where $\mathbb{1}^{A(B)}$ is the identity matrix in $\mathcal{H}^{A(B)}$. $A \otimes \mathbb{1}^B$ and $\mathbb{1}^A \otimes B$ are the operators in the entire Hilbert space but only acting in their respective subspaces.

2.2.1 Two spins

Consider a two-spin system. The vector spin operators of the two spins are denoted by $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$, and the total vector spin operator is:

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 = (\hat{S}_{1x} + \hat{S}_{2x}, \hat{S}_{1y} + \hat{S}_{2y}, \hat{S}_{1z} + \hat{S}_{2z})^T, \quad (2.38)$$

with the total component spin operator $\hat{S}_k = \hat{S}_{1k} + \hat{S}_{2k}$ for all $k \in \{x, y, z\}$. Then, we have:

$$\begin{aligned} \hat{S}^2 &= (\hat{S}_{1x} + \hat{S}_{2x})^2 + (\hat{S}_{1y} + \hat{S}_{2y})^2 + (\hat{S}_{1z} + \hat{S}_{2z})^2 \\ &= \hat{S}_1^2 + \hat{S}_2^2 + 2 \sum_{k=x,y,z} \hat{S}_{1k} \hat{S}_{2k}. \end{aligned} \quad (2.39)$$

Still as $[\hat{S}^2, \hat{S}_z] = 0$, the simultaneous eigenstates of $\hat{S}^2$ and $\hat{S}_z$ are denoted by $|S, M_S\rangle$, where S and M_S are the total spin quantum number and the total spin projection quantum number, respectively. Besides, the entire spin space of the two-spin system can be spanned by the tensor products of the eigenstates of $\hat{S}_1^2$ ($\hat{S}_{1z}$) and $\hat{S}_2^2$ ($\hat{S}_{2z}$), which are denoted by $|s_1 s_2, m_{s_1} m_{s_2}\rangle$. It is important to

2.2. Addition of spin

notice that $[\hat{S}^2, \hat{S}_{1z}] \neq 0$ and $[\hat{S}^2, \hat{S}_{2z}] \neq 0$, such that $|S, M_S\rangle$ is not equivalent to $|s_1 s_2, m_{s_1} m_{s_2}\rangle$. But $|S, M_S\rangle$ can be expanded in terms of $|s_1 s_2, m_{s_1} m_{s_2}\rangle$:

$$\begin{aligned} |S, M_S\rangle &= \sum_{m_{s_1}, m_{s_2}} |s_1 s_2, m_{s_1} m_{s_2}\rangle \langle s_1 s_2, m_{s_1} m_{s_2} | S, M_S \rangle \\ &= \sum_{m_{s_1}, m_{s_2}} C_{m_{s_1} m_{s_2}}^{SM_S} |s_1 s_2, m_{s_1} m_{s_2}\rangle, \end{aligned} \quad (2.40)$$

where $C_{m_{s_1} m_{s_2}}^{SM_S} = \langle s_1 s_2, m_{s_1} m_{s_2} | S, M_S \rangle$ is the so-called Clebsch-Gordan coefficient. One will find that $C_{m_{s_1} m_{s_2}}^{SM_S}$ vanishes unless $M_S = m_{s_1} + m_{s_2}$ and $|s_1 - s_2| \leq S \leq s_1 + s_2$. For a two-spin system composed of two electrons, S is allowed to be 0 (with $M_S = 0$) or 1 (with $M_S = -1, 0, 1$). Thus, there are four eigenstates of $\hat{S}^2$, conventionally known as a singlet state for $S = 0, M_S = 0$ denoted by $|S\rangle$ and three triplet states for $S = 1$ denoted by $|T_-\rangle$ for $M_S = -1$, $|T_0\rangle$ for $M_S = 0$ and $|T_+\rangle$ for $M_S = 1$. They can be represented as:

$$\begin{aligned} |S\rangle &= \frac{1}{\sqrt{2}} |\uparrow\downarrow\rangle - \frac{1}{\sqrt{2}} |\downarrow\uparrow\rangle, \\ |T_0\rangle &= \frac{1}{\sqrt{2}} |\uparrow\downarrow\rangle + \frac{1}{\sqrt{2}} |\downarrow\uparrow\rangle, \\ |T_+\rangle &= |\uparrow\uparrow\rangle, \\ |T_-\rangle &= |\downarrow\downarrow\rangle, \end{aligned} \quad (2.41)$$

where the arrow-denoted states refer to $|s_1 s_2, m_{s_1} m_{s_2}\rangle$ with $\uparrow$ and $\downarrow$ indicating $m_s = +1/2$ and $m_s = -1/2$ respectively. Note that the spin vectors of the two electrons are precisely anti-parallel when they are in the singlet state. One finds that $\langle T_0 | \hat{S}_z^2 | T_0 \rangle = 0$ and $\langle T_0 | (\hat{S}_x^2 + \hat{S}_y^2) | T_0 \rangle = 2 = S(S+1)$, but $\langle T_0 | \hat{S}_j | T_0 \rangle = 0$ for all $j \in \{x, y, z\}$. This means that the electron spin vectors are parallel in the $|T_0\rangle$ state as an eigenstate (determined) for $\hat{S}_z$, but have random directions in the xy -plane. Such uncertainty in quantum mechanics - we cannot determine both $\hat{S}_z$ and $\hat{S}_{x(y)}$ (operators that do not commute) simultaneously - is also valid for a composite of the elementary particles such as the two-electron system.

2.2.2 The 2π rotation for multiple spins

In a radical pair, apart from the two unpaired electrons, the nuclear spins must be taken into account, as the spin interactions among the electron and nuclear spins are significant to the radical pair spin dynamics. The 2π rotation operator in equation (2.34) will be shown valid for such multiple spin system with a total spin quantum number S and a total spin projection quantum number M_S , consisting of integer (e.g. ^{14}N) and half-integer (e.g. the electrons and ^1H) spins ($s_1 s_2 \dots s_N, m_{s_1} m_{s_2} \dots m_{s_N}$). The allowed S ranges from the minimum positive combination of $s_1, s_2, \dots, s_N$ to the largest $s_1 + s_2 + \dots + s_N$. Then, one will realize that whether S is integer or half-integer is only related to the parity of the number of the half-integer spins (i.e. odd number of half-integer spins give a half-integer S , whereas even number of half-integer spins give an integer S). An arbitrary spin ket is always able to be expanded in terms of the various eigenstates of $\hat{S}^2$:

$$|\alpha\rangle = \sum_{S, M_S, \{\gamma\}} c_{S^{\{\gamma\}}, M_S}^{\alpha} |S^{\{\gamma\}}, M_S\rangle, \quad (2.42)$$

where $\{\gamma\}$ denote an aggregate of the additional quantum number γ for the total spin S , which is necessarily introduced for a system includes more than two spins. The rotation operator for every element $|S^{\{\gamma\}}, M_S\rangle$ turns out to be the same, following the analogous algebra in Section 2.1.2. The representation of the rotation operator for a multiple spin system is obtained:

$$\mathcal{D}_{(\mathbf{n}, 2\pi)} = (-1)^{N_{\text{half}}} \hat{\mathbb{1}}, \quad (2.43)$$

where N_{half} is the number of half-integer spins. The 2π rotation operator is an identity matrix for a spin system with even number of half-integer spins, and it becomes an identity matrix multiplied by -1 for a spin system with odd number of half-integer spins.

2.2.3 The spin states of a radical pair

Throughout this thesis, the photo-induced radical pair is supposed to be formed in an electronic spin singlet state in order to preserve the total spin angular momentum of two electrons in a closed shell - the electron transfer is supposed to be so fast that any potential spin magnetic interaction within the transfer process does not have enough time to make an appreciable change to the spin state of the two electrons. As well as the electronic spins, the nuclear spin subspaces must be included in the entire radical pair spin space, as the electron-nuclear spin interactions are critical for the spin evolution of the radical pair. An important assumption is that the nuclear spin state is in equilibrium when the radical pair is initialized such that the nuclear spins are totally mixed. Therefore, the nuclear spin state is a completely random ensemble in which populations of all the basis states are equal to each other and the nuclear spin coherences among these states are completely absent. This totally mixed nuclear spin state cannot be represented by a ket which only accounts for a pure state. Instead, the identity matrix divided by the dimension of the nuclear spin space, as the density matrix specifically for the totally mixed state at equilibrium, represents the initial nuclear spin state $\rho_{n(0)}$:

$$\rho_{n(0)} = \frac{1}{Z^1 \times Z^2} \mathbb{1}_n^1 \otimes \mathbb{1}_n^2 = \frac{1}{Z} \mathbb{1}_n, \quad (2.44)$$

where the identity matrices, $\mathbb{1}_n^1$ and $\mathbb{1}_n^2$, respectively describe the nuclear spin spaces of radical 1 and 2 with dimensions of Z^1 and Z^2 , such that the entire nuclear spin dimension of the radical pair $Z = Z^1 \times Z^2$, and the nuclear spin space $\mathbb{1}_n = \mathbb{1}_n^1 \otimes \mathbb{1}_n^2$. Z^i with $i = 1, 2$ is calculated as:

$$Z^i = \prod_{p=1}^{N_i} (2I_{i(p)} + 1), \quad (2.45)$$

where $I_{i(p)}$ denotes the spin quantum number of the p -th nucleus in radical i . Now, the initial spin state of the radical pair is obtained as:

$$\rho_{(0)} = \rho_{e(0)} \otimes \rho_{n(0)} = \frac{1}{Z} |\text{S}\rangle \langle \text{S}| \otimes \mathbb{1}_n, \quad (2.46)$$

where $\rho_{e(0)}$ denotes the two unpaired electrons that are in singlet state when the radical pair is formed.

Projection operator

The spin state of the radical pair evolves under the spin interactions, and meanwhile, the recombination of the radicals is selective on the spin state (i.e. radical pairs in singlet or triplet states are normally considered to recombine to different reaction products, namely the singlet product or the triplet product) [52]. Such spin selective reactions are realized by the projection operators in the Haberkorn quantum master equation [87], which will be discussed at detail in Section 2.4. The projection operators are linear operators. Specifically for a radical pair reaction, the singlet and triplet projection operators, $\hat{P}^{\text{S}}$ and $\hat{P}^{\text{T}}$, are particularly significant. They are written:

$$\begin{aligned} \hat{P}^{\text{S}} &= |\text{S}\rangle \langle \text{S}| \otimes \mathbb{1}_n, \\ \hat{P}^{\text{T}} &= \sum_{m=+,0,-} |\text{T}_m\rangle \langle \text{T}_m| \otimes \mathbb{1}_n. \end{aligned} \quad (2.47)$$

The action of $\hat{P}^{\text{S}}$ and $\hat{P}^{\text{T}}$ projects the electron spin state onto its singlet or triplet subspaces. The probability of finding the singlet or triplet state in the spin state of the radical pair at some moment t is:

$$P_{(t)}^{\text{S(T)}} = \text{Tr}\{\hat{P}^{\text{S(T)}} \rho_{(t)}\}, \quad (2.48)$$

where $\text{Tr}\{\dots\}$ denotes the trace. Note that the the initial singlet state of the radical pair can be written in terms of the singlet projection operator, $\rho_{(0)} = \frac{1}{Z} \hat{P}^{\text{S}}$.

2.2.4 Exchange of the electron spins

In a radical pair, the two unpaired electrons are localized in their respective radicals. Thus, the overlap of the two electrons' spatial wavefunctions is negligible. Note that this small overlap for a radical pair is characterized by the exchange interaction as a perturbation, like other spin magnetic interactions, to the electronic interactions. Therefore, the two electrons can be appropriately regarded as distinguishable [88]. Nevertheless, when the radical pair recombines, the two electrons will be stabilized in the same chemical environment, returning their indistinguishable property. This will give rise to a total anti-symmetric wave function composed of either a symmetric spatial wavefunction and an anti-symmetric spin wave function (i.e. the singlet reaction product Φ_S) or an anti-symmetric spatial wavefunction and a symmetric spin wave function (i.e. the triplet reaction product Φ_T). Therefore, the spin selective reaction can be viewed as the symmetrization or the anti-symmetrization of a generic spin state of the two electrons. The symmetrization $\hat{Q}_S$ and the anti-symmetrization $\hat{Q}_A$ operators can be written as:

$$\begin{aligned}\hat{Q}_S &= \frac{1}{2}(\mathbb{1} + \hat{P}_{21}) = \frac{3}{4}\mathbb{1} + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2, \\ \hat{Q}_A &= \frac{1}{2}(\mathbb{1} - \hat{P}_{21}) = \frac{1}{4}\mathbb{1} - \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2,\end{aligned}\tag{2.49}$$

where $\hat{P}_{21}$ is the permutation operator, which exchanges the spin states of the two electrons: $\hat{P}_{21}(|v\rangle_{(1)} \otimes |\mu\rangle_{(2)}) = |\mu\rangle_{(1)} \otimes |v\rangle_{(2)}$. $\hat{P}_{21}$ is represented as [85]:

$$\hat{P}_{21} = \frac{1}{2}\mathbb{1} + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2.\tag{2.50}$$

Note that $\hat{Q}_S$ and $\hat{Q}_A$ are not unitary, though their summation turns out to be $\mathbb{1}$. For a state that is already symmetric/anti-symmetric, the operation of anti-symmetrization/symmetrization will be physically meaningless, as $\hat{Q}_A|\alpha_S\rangle = 0$; $\hat{Q}_S|\alpha_A\rangle = 0$ ($|\alpha_S\rangle/|\alpha_A\rangle$ denotes a symmetric/anti-symmetric state). In terms of the spin selective reactions of a radical pair, $\hat{Q}_A$ and $\hat{Q}_S$ are equivalent to the

projection operators $\hat{P}^S$ and $\hat{P}^T$ in equation (2.47). Thus,

$$\begin{aligned}\hat{P}^S &= \frac{1}{4}\hat{\mathbb{1}} - \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2, \\ \hat{P}^T &= \frac{3}{4}\hat{\mathbb{1}} + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2.\end{aligned}\tag{2.51}$$

2.3 The spin interactions in a radical pair

In quantum mechanics, the Hamiltonian operator corresponding to the total energy of a system, is the generator of an infinitesimal time evolution of the state:

$$\hat{\mathcal{U}}_{(\delta t)} = 1 - i\hat{H}\delta t.\tag{2.52}$$

This can be inferred from the Schrödinger equation [85]. If $\hat{H}$ is time-independent, a finite time evolution can be straightforwardly generalized as:

$$\hat{\mathcal{U}}_{(t)} = e^{-i\hat{H}t}.\tag{2.53}$$

The magnetic field effect on a radical pair is understood through its modulation on the time evolution of the radical pair spin state. Then, it is necessary to assure the Hamiltonians of the significant spin interactions.

2.3.1 Zeeman interaction

In the presence of an external magnetic field, lines in the spectra of atoms are split into a number of polarized components [89]. This is due to the so-called Zeeman interaction between the electron magnetic dipole and the static magnetic field, characterized by $\hat{H}_Z$:

$$\hat{H}_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B} = (g_l \frac{\mu_B}{\hbar} \hat{\mathbf{L}} + g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}}) \cdot \mathbf{B}.\tag{2.54}$$

$\hat{H}_Z$ describes the coupling of the electron magnetic moments with the external magnetic field. It is important to note that in organic radicals, there normally exist asymmetric ligand fields which will quench the orbital momentum (i.e. $\langle \hat{\mathbf{L}} \rangle = 0$).

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Besides, because of the lack of heavy atoms in organic radicals, the spin-orbit coupling $\propto \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, which accounts for the exchange between the electron orbital and spin angular momentum, is negligible. Therefore, only the $\hat{\mathbf{S}} \cdot \mathbf{B}$ part that significantly contributes to the spin dynamics of a radical pair. Then, $\hat{H}_Z$ is re-written as:

$$\hat{H}_Z = g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}} \cdot \mathbf{B} = -\gamma_e \hat{\mathbf{S}} \cdot \mathbf{B}. \quad (2.55)$$

One will find that the time evolution attributed to $\hat{H}_Z$ is equivalent to the rotation around the direction $\mathbf{n}$ of the static magnetic field ($\mathbf{B} = B \mathbf{n}$):

$$\hat{\mathcal{U}}_{Z(t)} = e^{-i\hat{H}_Z t} = e^{-i(-\gamma_e \hat{\mathbf{S}} \cdot \mathbf{B})t} = e^{-i(\hat{\mathbf{S}} \cdot \mathbf{n})\omega_0 t} = \mathcal{D}_{(\mathbf{n}, \omega_0 t)}, \quad (2.56)$$

where $\omega_0 = -\gamma_e B$ is angular frequency of such rotation. Then, the frequency is $\nu_L = \omega_0/2\pi$, which is the so-called Larmor frequency, and the Larmor period is $1/\nu_L$. A rough guide for the radical pair lifetime is that the radical pair should live for at least as long as one Larmor period of the magnetic field, such that it can possibly produce appreciable modulation of the spin dynamics of the radical pair before recombination. For Earth's magnetic field of $50 \mu\text{T}$, the Larmor period is around 710 ns , whereby it is promising to have magnetic effect on a radical pair with a lifetime $\sim 1 \mu\text{s}$.

2.3.2 Hyperfine interaction

The hyperfine splitting arises from the energy of the interaction of the electron spin with the nuclear spin. The Hamiltonian for the hyperfine interactions is:

$$\hat{H}_{\text{hf}} = -\gamma_e \frac{2\mu_0 g_N \mu_N}{3} \delta_{(\mathbf{r})}^3 \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} - \gamma_e \frac{\mu_0 g_N \mu_N}{4\pi |\mathbf{r}|^3} (3(\hat{\mathbf{S}} \cdot \mathbf{n}_r)(\hat{\mathbf{I}} \cdot \mathbf{n}_r) - \hat{\mathbf{S}} \cdot \hat{\mathbf{I}}), \quad (2.57)$$

where g_N denotes the nuclear g -factor, μ_N is the nuclear magneton, μ_0 denotes the vacuum permeability, and $\mathbf{r}$ denotes the joining vector which connects positions of the electron and the nucleus with $\mathbf{n}_r = (n_x, n_y, n_z)^\top$ the unit vector in the direction of $\mathbf{r}$. The first term of $\hat{H}_{\text{hf}}$ indicates the Fermi contact interaction [90], which

requires the electron to have some s-orbital character (i.e. the spatial wavefunction of the electron, $\psi_{(\mathbf{x})}$, has non-zero amplitude to be at the nucleus). The second term of $\hat{H}_{\text{hf}}$ indicates the dipole-dipole interaction arising from the electron spin magnetic dipole interacting with the magnetic field generated by the nuclear spin dipole at a finite distance. This contributes to the anisotropic property of the hyperfine interaction. For convenience, $\hat{H}_{\text{hf}}$ is written in tensor form:

$$\hat{H}_{\text{hf}} = -\gamma_e \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{I}} = -\gamma_e \sum_{\substack{k,j \\ =x,y,z}} A_{kj} \hat{S}_k \hat{I}_j, \quad (2.58)$$

where $\mathbf{A}$ is the so-called hyperfine tensor with 9 components [91],

$$A_{kj} = \delta_{kj} a_0 + \frac{\mu_0 g_N \mu_N}{4\pi} \int \psi_{(\mathbf{x})}^* \frac{3 n_k n_j - \delta_{kj}}{|\mathbf{r}|^3} \psi_{(\mathbf{x})} d^3 \mathbf{x}, \quad (2.59)$$

with $a_0 = \int \psi_{(\mathbf{x})}^* \frac{2\mu_0 g_N \mu_N}{3} \delta_{(\mathbf{r})}^3 \psi_{(\mathbf{x})} d^3 \mathbf{x}$, the isotropic hyperfine constant. The hyperfine tensor can be obtained from a DFT (density functional theory) calculation. Appendix A summarizes the hyperfine tensors in the radicals that are significant for radical-pair based magnetoreception.

Note that $\hat{H}_Z$ of the Zeeman interaction commutes with $\hat{S}^2$, the operator that characterizes the total spin angular momentum of the two electrons, whereby the electronic singlet state, as an eigenstate of $\hat{S}^2$, cannot evolve solely with $\hat{H}_Z$ (note that here we ignore the negligible g -value differen in two organic radicals). This can also be understood by remembering that the singlet state, as a spherically symmetric state, will not change after any Zeeman interaction induced rotation represented by the $\mathcal{D}_{(\mathbf{n}, \omega_0 t)}$ in equation (2.56). It is the hyperfine interactions of the electrons with the nuclei in respective radicals (often with a strength of several hundred microtesla in a FAD-based radical pair formed in cryptochromes) that are responsible for the singlet-triplet interconversion, whereas a weak external magnetic field, such as Earth's magnetic field $\sim 50 \mu\text{T}$, shows its effect by

modulating the singlet-triplet interconversion. Such modulation is related to the field direction relative to the quantized axis of the hyperfine interactions, which is thus considered as the origin of the avian navigational ability of detecting the direction of Earth's magnetic field. The anisotropic weak magnetic field effect will be discussed at detail in Chapter 3.

2.3.3 Inter-radical interactions

Apart from the interactions of the electron spins with the external magnetic field and the nuclear spins, there exist inter-radical interactions (i.e. the spin couplings between the two electrons one in each radical) participating in the spin dynamics of a radical pair.

Exchange interaction

Often, the two radicals (radical 1 and 2) of a radical pair are considered electronically isolated from each other. The two electrons are localized, one in each radical. The total electronic Hamiltonian of a radical pair is the direct sum of those of the two radicals:

$$\hat{H}_{\text{tot}} = \hat{H}_A \oplus \hat{H}_B = \begin{pmatrix} \hat{H}_A & 0 \\ 0 & \hat{H}_B \end{pmatrix}, \quad (2.60)$$

where $\hat{H}_{A(B)}$ describes the internal electronic interactions of one of the two radicals, with eigenfunctions $\varphi_{A(\mathbf{x})}$ ($\varphi_{B(\mathbf{x})}$). The regions of each radical spanned by the eigenfunctions are represented as $\mathbb{R}_A$ and $\mathbb{R}_B$ respectively ($\mathbb{R}_A \cap \mathbb{R}_B = 0$). For two localized non-overlapping electrons, they can be treated as distinguishable particles [88], such that the spatial wavefunction of the radical pair can be written in a separable form $\varphi_{A(\mathbf{x}_1)}\varphi_{B(\mathbf{x}_2)}$ where $\mathbf{x}_1 \in \mathbb{R}_A$ and $\mathbf{x}_2 \in \mathbb{R}_B$. However, in reality, the two radicals can interact with each other, e.g. the electronic interactions of the unpaired electron in one radical with the nuclei and the unpaired electron in the other radical. Such inter-radical interactions give rise to the non-zero off-diagonal

elements in $\hat{H}_{\text{tot}}$ characterized by Δ as a perturbation [92]. $\hat{H}_{\text{tot}} = \hat{H}_0 + \delta\hat{H}$ with

$$\hat{H}_0 = \begin{pmatrix} \hat{H}_A & 0 \\ 0 & \hat{H}_B \end{pmatrix} \text{ and } \delta\hat{H} = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix}. \quad (2.61)$$

Now, the small overlap of the regions of the two radicals (i.e. $\mathbb{R}_A \cap \mathbb{R}_B = \Delta\mathbb{R}_{AB} \neq 0$) must be taken into account. The total wavefunction of the two electrons is represented in an anti-symmetric form, $\phi_+ \cdot \chi_{\text{singlet}}$ or $\phi_- \cdot \chi_{\text{triplet}}$, where χ_{singlet} and χ_{triplet} denote the spin singlet and triplet states, and $\phi_{\pm}$ denote the electronic spatial wavefunction written as:

$$\phi_{\pm} = \frac{N_{\pm}}{\sqrt{2}} (\varphi_{A(\mathbf{x}_1)} \varphi_{B(\mathbf{x}_2)} \pm \varphi_{B(\mathbf{x}_1)} \varphi_{A(\mathbf{x}_2)}), \quad (2.62)$$

with $N_{\pm}$ the normalization factor. $N_{\pm}$ will be obtained through:

$$\begin{aligned} & \iint_{\mathbb{R}_A \cup \mathbb{R}_B} \phi_{\pm}^* \phi_{\pm} d^3\mathbf{x}_1 d^3\mathbf{x}_2 \\ &= \iint_{\mathbb{R}_A \cup \mathbb{R}_B} \frac{N_{\pm}^2}{2} (|\varphi_{A(\mathbf{x}_1)} \varphi_{B(\mathbf{x}_2)}|^2 + |\varphi_{B(\mathbf{x}_1)} \varphi_{A(\mathbf{x}_2)}|^2 \pm \\ & \quad 2 \varphi_{A(\mathbf{x}_1)}^* \varphi_{B(\mathbf{x}_1)} \varphi_{B(\mathbf{x}_2)}^* \varphi_{A(\mathbf{x}_2)}) d^3\mathbf{x}_1 d^3\mathbf{x}_2 \\ &= \frac{N_{\pm}^2}{2} (1 + 1 \pm 2 \int_{\Delta\mathbb{R}_{AB}} \varphi_{A(\mathbf{x}_1)}^* \varphi_{B(\mathbf{x}_1)} d^3\mathbf{x}_1 \int_{\Delta\mathbb{R}_{AB}} \varphi_{B(\mathbf{x}_2)}^* \varphi_{A(\mathbf{x}_2)} d^3\mathbf{x}_2) \\ &= \frac{N_{\pm}^2}{2} (2 \pm 2|\alpha_{AB}|^2) \\ &= 1, \end{aligned} \quad (2.63)$$

with $\alpha_{AB} = \int_{\Delta\mathbb{R}_{AB}} \varphi_{A(\mathbf{x})}^* \varphi_{B(\mathbf{x})} d^3\mathbf{x}$, the overlap of the eigenfunctions $\varphi_{A(\mathbf{x})}$ and $\varphi_{B(\mathbf{x})}$. Then, $N_{\pm} = \frac{1}{\sqrt{1 \pm |\alpha_{AB}|^2}}$. The energy correction from the perturbative inter-radical interactions is related to the (anti-)symmetry of the spatial wavefunction:

$$\Delta_{\pm} = \iint_{\mathbb{R}_A \cup \mathbb{R}_B} \phi_{\pm}^* \Delta \phi_{\pm} d^3\mathbf{x}_1 d^3\mathbf{x}_2 = \frac{C \pm J}{1 \pm |\alpha_{AB}|^2}, \quad (2.64)$$

with

$$\begin{aligned} C &= \iint_{\mathbb{R}_A \cup \mathbb{R}_B} \varphi_{A(\mathbf{x}_1)}^* \varphi_{B(\mathbf{x}_2)}^* \Delta \varphi_{A(\mathbf{x}_1)} \varphi_{B(\mathbf{x}_2)} d^3\mathbf{x}_1 d^3\mathbf{x}_2 \\ J &= \iint_{\mathbb{R}_A \cup \mathbb{R}_B} \varphi_{A(\mathbf{x}_1)}^* \varphi_{B(\mathbf{x}_2)}^* \Delta \varphi_{B(\mathbf{x}_1)} \varphi_{A(\mathbf{x}_2)} d^3\mathbf{x}_1 d^3\mathbf{x}_2. \end{aligned} \quad (2.65)$$

2.3. The spin interactions in a radical pair

Here, C characterizes the Coulomb interaction (Coulomb integral) between the two radicals, e.g. the repulsive potential for the electron at radical A in an electric field created by electron at radical B. J , normally known as the exchange integral, has no simple physical interpretation, which arises entirely due to the anti-symmetry requirement for the total wavefunction of the two electrons. Δ_+ with $+J$ is the spatially symmetric (so the spin singlet) solution and Δ_- with $-J$ is the spatially anti-symmetric (so the spin triplet) solution. Thus, a spin Hamiltonian, with the singlet and three degenerate triplet states being the four eigenstates, can be constructed to describe the so-called exchange interaction characterized by J . Such Hamiltonian can be inferred from the permutation operator in equation (2.50) which has:

$$\hat{P}_{21}|S\rangle = -|S\rangle, \quad \hat{P}_{21}|T\rangle = |T\rangle. \quad (2.66)$$

Thus, the exchange interaction Hamiltonian is represented as:

$$\hat{H}_{\text{ex}} = -J\hat{P}_{21} = -J\left(\frac{1}{2}\mathbb{1} + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2\right). \quad (2.67)$$

Note that here we have approximately taken α_{AB} as zero for an organic radical pair. J is usually assumed to have exponential form:

$$J = J_0 e^{-\beta r} \quad (2.68)$$

where β is $\sim 14 \text{ nm}^{-1}$ as a range parameter for radicals embedded in a protein [93, 94], and J_0 is complicatedly dependent on the electronic properties of the radicals and it is difficult to calculate with any accuracy.

Dipolar interaction

The interaction between the two electron spin dipoles is characterized by the dipolar interaction:

$$\hat{H}_{\text{dip}} = -\gamma_e \frac{2}{3} D_{(|\mathbf{r}_{12}|)} \left(3(\hat{\mathbf{S}}_1 \cdot \mathbf{n}_{\mathbf{r}_{12}})(\hat{\mathbf{S}}_2 \cdot \mathbf{n}_{\mathbf{r}_{12}}) - \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \right), \quad (2.69)$$

where $\mathbf{r}_{12}$ is the vector joining the centers of spin densities, $\mathbf{n}_{r_{12}}$ is the unit vector along the direction of $\mathbf{r}_{12}$, and $D_{(|\mathbf{r}_{12}|)} = -\frac{3\mu_0 g_e \mu_B}{8\pi |\mathbf{r}_{12}|^3}$ characterizes the strength of the dipolar interaction. $\mathbf{n}_{12}$ can be considered as the unit vector along the z -axis after two sequential rotations, firstly around the y -axis by the polar angle θ_D and then around the z -axis by the azimuthal angle ϕ_D :

$$\mathbf{n}_{r_{12}} = R_D \mathbf{n}_z = R_{(z, \phi_D)} R_{(y, \theta_D)} \mathbf{n}_z. \quad (2.70)$$

As is in equation (2.31), the rotation R_D can be attributed inversely to the spin vector operator, such that:

$$\hat{\mathbf{S}}_{1(2)} \cdot \mathbf{n}_{r_{12}} = (R_D^{-1} \hat{\mathbf{S}}_{1(2)})^\top \mathbf{n}_z = \sum_{j=x,y,z} (R_D^{-1})_{zj} \hat{S}_{1(2)j}. \quad (2.71)$$

Then, $\hat{H}_{\text{dip}}$ in equation (2.69) can be written in the tensor form:

$$\begin{aligned} \hat{H}_{\text{dip}} &= -\gamma_e (R_D^{-1} \hat{\mathbf{S}}_1)^\top \tilde{\mathbf{D}} (R_D^{-1} \hat{\mathbf{S}}_2) \\ &= -\gamma_e \hat{\mathbf{S}}_1^\top (R_D \tilde{\mathbf{D}} R_D^{-1}) \hat{\mathbf{S}}_2 \\ &= -\gamma_e \hat{\mathbf{S}}_1 \cdot \mathbf{D} \cdot \hat{\mathbf{S}}_2, \end{aligned} \quad (2.72)$$

where

$$\begin{aligned} \tilde{\mathbf{D}} &= \frac{2}{3} D_{(|\mathbf{r}_{12}|)} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \\ \mathbf{D} &= R_{(z, \phi_D)} R_{(y, \theta_D)} \tilde{\mathbf{D}} R_{(y, -\theta_D)} R_{(z, -\phi_D)}. \end{aligned} \quad (2.73)$$

Note that $\hat{H}_{\text{dip}}$ commutes with $\hat{S}^2$. Thus, the singlet and three triplet states are also the eigenstates of $\hat{H}_{\text{dip}}$, and the corresponding energy eigenvalues are 0 for $|\text{S}\rangle$, $-\frac{2}{3} D_{(|\mathbf{r}_{12}|)}$ for $|\text{T}_0\rangle$, and $\frac{1}{3} D_{(|\mathbf{r}_{12}|)}$ for $|\text{T}_\pm\rangle$ (here the $\mathbf{r}_{12}$ is set to be along the quantization axis).

Inter-radical interactions as a barrier & their cancellation

The energy gaps between the singlet and triplet states brought by the inter-radical interactions often obstruct the interconversion of the singlet and triplet states of

2.3. The spin interactions in a radical pair

a radical pair. This can be illustrated by a two-level system,

$$\hat{H}_{2l} = \begin{pmatrix} \omega_1 & q \\ q & \omega_2 \end{pmatrix}, \quad (2.74)$$

where ω_1 and ω_2 denote the energies for the inter-electron interactions, and q indicates the hyperfine interaction that is responsible for the singlet-triplet interconversion. The projection operators are written:

$$\hat{P}^S = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \hat{P}^T = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.75)$$

Suppose the initial state is the singlet state (i.e. $\rho_{(0)} = \hat{P}^S$), then according to equation (2.48) the time-dependent probability of finding the triplet state is:

$$P_{(t)}^T = \text{Tr}\{\hat{P}^T \rho_{(t)}\} = \frac{q^2}{\omega_{12}^2 + q^2} \sin^2(\sqrt{\omega_{12}^2 + q^2} t), \quad (2.76)$$

where $\rho_{(t)}$ is obtained by solving the Liouville-von Neumann equation which will be introduced in Section 2.4, and $\omega_{12} = |\omega_1 - \omega_2|$ is the energy gap induced by the inter-radical interactions. The larger the energy gap is, the smaller is the amplitude of $P_{(t)}^T$, meaning that the singlet-triplet interconversion becomes less efficient. It was suggested [93] that such obstruction of spin dynamics can be removed if $\omega_{12} = 0$ (i.e. the singlet and triplet states share the same energy in the inter-radical interactions). Computational study [93] shows that the restoration of the singlet-triplet interconversion efficiency can be partially accomplished either by having $D_{(|\mathbf{r}_{12}|)} = -3J$ or $D_{(|\mathbf{r}_{12}|)} = 6J$ (known as the “ J/D cancellation”), which is reasonable for a radical pair with the radical-radical separation ranging from 1.8 to 2.2 nm. However, this cancellation seems unlikely for the avian magnetoreception. Electron paramagnetic resonance experiments [79] suggest that $J \ll D_{(|\mathbf{r}_{12}|)}$ for the $[\text{FAD}^{\bullet-} \text{ TrpH}^{\bullet+}]$ radical pair in avian cryptochromes. A recent theoretical study [95] suggested that J/D cancellation is not efficient in FAD-based radical pairs.

2.4 Spin-selective reactions

The time-dependence of the spin state of a radical pair is described by the Liouville–von Neumann equation:

$$\frac{d\rho(t)}{dt} = -i[\hat{H}, \rho(t)]. \quad (2.77)$$

If the Hamiltonian is time-independent, $\rho(t)$ can be obtained:

$$\rho(t) = \mathcal{U}(t) \rho(0) \mathcal{U}(t)^\dagger, \quad (2.78)$$

where the time-evolution operator $\mathcal{U}(t) = e^{-i\hat{H}t}$ as is defined in equation (2.53). $\mathcal{U}(t)$ is unitary, so such that the trace of $\rho(t)$ is conserved. However, the chemical reactions of the radicals cause the trace to decay. Then, the reactants and products are characterized by respective density matrices. In a spin-coherent radical pair, the reactions can be spin-selective. Not only will the selected projected proportion of the radical pair (e.g. the singlet radical pair, $\hat{P}^S \rho(t) \hat{P}^S$, selected for recombination) decay, but the coherences between the selected states (e.g. $\hat{P}^S \rho(t) \hat{P}^T$) also need to disappear when the reaction finishes [87]. Normally, the chemical reaction is represented by a non-unitary operation characterized by the reaction operator $\hat{K}$, which can be included in equation (2.77):

$$\frac{d\rho(t)}{dt} = -i[\hat{H}, \rho(t)] - \{\hat{K}, \rho(t)\}, \quad (2.79)$$

where $\{A, B\} = AB + BA$. Throughout this thesis, the spin-selective reaction operators are formulated according to Haberkorn [87]. The reaction operators of the singlet and triplet recombination are:

$$\hat{K}_S = \frac{k_S}{2} \hat{P}^S, \quad \hat{K}_T = \frac{k_T}{2} \hat{P}^T, \quad (2.80)$$

where k_S and k_T are first order rate constants. Moreover, the spin-independent reactions in radical pairs, such as the deprotonation of $\text{TrpH}^{\bullet+}$ radical in avian cryptochromes, are represented as

$$\hat{K}_F = \frac{k_F}{2} \hat{\mathbb{1}}. \quad (2.81)$$

2.4.1 Symmetric reaction

Symmetric reaction approximation [54], $k_S = k_T$, is often used to evaluate the potential ability of a candidate radical pair to sense the external magnetic field. Besides, this approximation helps to simplify the calculation, as the spin-selective reaction operators add to give the identity operator which commutes with the density matrix:

$$\{\hat{K}_S + \hat{K}_T, \rho_{(t)}\} = \left\{\frac{k}{2}(\hat{P}^S + \hat{P}^T), \rho_{(t)}\right\} = \left\{\frac{k}{2}\hat{\mathbb{1}}, \rho_{(t)}\right\} = k\rho_{(t)}, \quad (2.82)$$

where $k = k_S = k_T$. Ignoring the spin-independent reactions and recalling equation (2.79), we obtain the solution for $\rho_{(t)}$:

$$\rho_{(t)} = \hat{\mathcal{U}}(t) \rho_{(0)} \hat{\mathcal{U}}^\dagger(t) e^{-kt}, \quad (2.83)$$

where the chemical reactions have been represented by a simple exponential decay. Thus, the radical pair lifetime, τ , is $1/k$. Now, the time-dependent probability of finding the singlet radical pair, $P_{(t)}^S$, is given in the eigenbasis of the spin Hamiltonian [54]:

$$\begin{aligned} P_{(t)}^S &= \text{Tr}\{\hat{P}^S \rho_{(t)}\} \\ &= \text{Tr}\left\{\frac{1}{Z} \hat{P}^S e^{-i\hat{H}t} \hat{P}^S e^{i\hat{H}t} e^{-kt}\right\} \\ &= \text{Tr}\left\{\frac{1}{Z} \sum_{m,n} \hat{P}^S |m\rangle \langle m| \hat{P}^S |n\rangle \langle n| e^{-i\omega_{mn}t} e^{-kt}\right\} \\ &= \frac{1}{Z} \sum_{m,n} |P_{mn}^S|^2 \cos(\omega_{mn}t) e^{-kt}, \end{aligned} \quad (2.84)$$

where $|m\rangle$ and $|n\rangle$ are eigenstates of $\hat{H}$ with energy eigenvalues ω_m and ω_n with units of $\text{rad} \cdot \text{s}^{-1}$, $P_{mn}^S = \langle m|\hat{P}^S|n\rangle$ and $\omega_{mn} = \omega_m - \omega_n$. Note that $P_{(t)}^S$ is real, since the imaginary part of $e^{i\omega_{mn}t}$ will be cancelled by interchanging m and n through the summation. In the context of radical pair based magnetoreception, the product yield of the spin-selective reactions quantifies the information that is

considered available for migratory birds to use, though it still remains unclear how birds exactly use it. The weak magnetic field affects the product yield through its modulation of the spin dynamics of the radical pair. Conventionally, the product yield of the singlet recombination (known as the singlet yield, Φ_S) is calculated to describe the magnetic field effect,

$$\Phi_S = \int_0^\infty k P_{(t)}^S dt = \frac{1}{Z} \sum_{m,n} |\hat{P}_{mn}^S|^2 f_{(\omega_{mn})}, \quad (2.85)$$

where $f_{(\omega_{mn})} = \frac{k^2}{k^2 + \omega_{mn}^2}$ is the Lorentzian function.

2.4.2 Asymmetric reaction

The symmetric reaction approximation has been variously applied to obtain preliminary computational predictions for a potential radical-based magnetic compass. However, we have to be more careful about the rate constants, k_S , k_T and k_F when modelling a realistic photo-induced radical pair. The calculation becomes more complicated now, as the reaction operators do not combine to the identity operator and they do not necessarily commute with the density matrix. In cryptochromes, $k_T = 0$ and $k_S, k_F \neq 0$ [53, 79]. One can still do the calculation in Hilbert space using the “General Method” in Ref [96], rather than stepping into Liouville space with squared dimensions that greatly increases the calculation pressure. The total reaction operator $\hat{K}$ is now written:

$$\hat{K} = \hat{K}_S + \hat{K}_F = \frac{k_S}{2} \hat{P}^S + \frac{k_F}{2} \hat{\mathbb{1}}, \quad (2.86)$$

which, combined with $\hat{H}$, gives a non-Hermitian operator $\hat{C} = \hat{H} - i\hat{K}$ with $\hat{C} \neq \hat{C}^\dagger$. Diagonalization of $\hat{C}$ and $\hat{C}^\dagger$ gives:

$$A^{-1} \hat{C} A = \hat{c}, \quad A^\dagger \hat{C}^\dagger (A^{-1})^\dagger = \hat{c}^*, \quad (2.87)$$

where we have used $(A^{-1} \hat{C} A)^\dagger = \hat{c}^* = A^\dagger \hat{C}^\dagger (A^{-1})^\dagger$. Note that a non-Hermitian operator does not necessarily have a set of orthogonal eigenstates, thus $A^{-1} \neq A^\dagger$.

2.5. Spin relaxation

The time-evolution operator $\mathcal{Q}_{(t)}$ is no longer unitary (i.e. $\mathcal{Q}_{(t)} = e^{-i\hat{C}t}$, $\mathcal{Q}_{(t)}^\dagger = e^{i\hat{C}^\dagger t}$, and $\mathcal{Q}_{(t)}^\dagger \neq \mathcal{Q}_{(t)}^{-1}$). Then, $P_{(t)}^S$ is obtained as:

$$\begin{aligned}
P_{(t)}^S &= \text{Tr}\{\hat{P}^S \mathcal{Q}_{(t)} \rho_{(0)} \mathcal{Q}_{(t)}^\dagger\} \\
&= \frac{1}{Z} \text{Tr}\{\hat{P}^S A A^{-1} e^{-i\hat{C}t} A A^{-1} \hat{P}^S (A^{-1})^\dagger A^\dagger e^{-i\hat{C}^\dagger t} (A^{-1})^\dagger A^\dagger\} \\
&= \frac{1}{Z} \text{Tr}\{\hat{P}^S A e^{-i\hat{C}t} X e^{i\hat{C}^* t} A^\dagger\} \\
&= \frac{1}{Z} \text{Tr}\{e^{-i\hat{C}t} X e^{i\hat{C}^* t} Y\} \\
&= \frac{1}{Z} \sum_{j,k} e^{-ic_j t} X_{jk} e^{ic_k^* t} Y_{kj},
\end{aligned} \tag{2.88}$$

where c_j is the j -th diagonal element of $\hat{C}$, c_k^* is the k -th diagonal element of $\hat{C}^*$, $X = A^{-1} \hat{P}^S (A^{-1})^\dagger$ and $Y = A^\dagger \hat{P}^S A$. Now, the singlet yield is:

$$\Phi_S = \frac{k_S}{Z} \sum_{j,k} X_{jk} Y_{kj} \int_0^\infty e^{i(c_k^* - c_j)t} dt = \frac{ik_S}{Z} \sum_{j,k} \frac{X_{jk} Y_{kj}}{c_k^* - c_j}. \tag{2.89}$$

The diagonalization of $\hat{C}$ and $\hat{C}^\dagger$ is computationally demanding and becomes prohibitive when the spin system has more than ~ 10 spins [96].

2.5 Spin relaxation

For a weak magnetic field, such as Earth's magnetic field ($\sim 50 \mu\text{T}$), to influence the spin dynamics of a radical pair, the coherence of the radical pair must live for a relatively long time (more than one Larmor period [97]) before reaching equilibrium where the spin correlation of the radical pair has died away and the external magnetic field has no further effect on the yield of the reaction product. However, in a realistic situation, various stochastic molecular motions, such as the rotational tumbling, modulate the magnetic spin interactions within radical pairs, which unavoidably results in spin relaxation causing the spin coherences and populations to relax towards equilibrium. In order to characterize such stochastic process, the spin Hamiltonian is separated into the static (unperturbed) part $\hat{H}_0$ and the dynamic part $\hat{H}_{1(t)}$.

2.5.1 Redfield approach

The Redfield approach [98] of describing the spin relaxation is widely used for a spin system that is weakly coupled to the environment, such that this method is pertinent to the radical pairs formed in cryptochromes with a constrained mobility. In the interaction picture (see Appendix C), the density matrix $\tilde{\rho}_{(t)}$ is transformed from that $\rho_{(t)}$ in the Schrödinger picture as:

$$\tilde{\rho}_{(t)} = e^{i\hat{H}_0 t} \rho_{(t)} e^{-i\hat{H}_0 t}, \quad (2.90)$$

which gives a sense that the time evolution from the static spin Hamiltonian has been excluded. The dynamical equation for $\tilde{\rho}_{(t)}$ can be written by recalling equation (2.77):

$$\begin{aligned} \frac{d\tilde{\rho}_{(t)}}{dt} &= \frac{d}{dt}(e^{i\hat{H}_0 t} \rho_{(t)} e^{-i\hat{H}_0 t}) \\ &= i\hat{H}_0 \tilde{\rho}_{(t)} - i\tilde{\rho}_{(t)} \hat{H}_0 + (e^{i\hat{H}_0 t} \frac{d\rho_{(t)}}{dt} e^{-i\hat{H}_0 t}) \\ &= i[\hat{H}_0, \tilde{\rho}_{(t)}] - i(e^{i\hat{H}_0 t} [\hat{H}_0 + \hat{H}_{1(t)}, \rho_{(t)}] e^{-i\hat{H}_0 t}) \\ &= i[\hat{H}_0, \tilde{\rho}_{(t)}] - i[e^{i\hat{H}_0 t} \hat{H}_0 e^{-i\hat{H}_0 t}, \tilde{\rho}_{(t)}] - i[e^{i\hat{H}_0 t} \hat{H}_{1(t)} e^{-i\hat{H}_0 t}, \tilde{\rho}_{(t)}] \\ &= -i[\hat{\tilde{H}}_{1(t)}, \tilde{\rho}_{(t)}], \end{aligned} \quad (2.91)$$

where $\hat{\tilde{H}}_{1(t)} = e^{i\hat{H}_0 t} \hat{H}_{1(t)} e^{-i\hat{H}_0 t}$. Then, $\tilde{\rho}_{(t)}$ can be expressed by integrating equation (2.91) with respect to time:

$$\tilde{\rho}_{(t)} = \tilde{\rho}_{(0)} - i \int_0^t [\hat{\tilde{H}}_{1(t')}, \tilde{\rho}_{(t')}] dt'. \quad (2.92)$$

Substituting this expression into equation (2.91), we obtain:

$$\begin{aligned} \frac{d\tilde{\rho}_{(t)}}{dt} &= -i[\hat{\tilde{H}}_{1(t)}, \tilde{\rho}_{(0)} - i \int_0^t [\hat{\tilde{H}}_{1(t')}, \tilde{\rho}_{(t')}] dt'] \\ &= -i[\hat{\tilde{H}}_{1(t)}, \tilde{\rho}_{(0)}] - \int_0^t [\hat{\tilde{H}}_{1(t)}, [\hat{\tilde{H}}_{1(t')}, \tilde{\rho}_{(t')}] dt'. \end{aligned} \quad (2.93)$$

It is assumed that each radical pair is supposed to relax independently, such that it is reasonable to take an ensemble average of all the Hamiltonians in equation

(2.93) [99, 100]. Given that $\hat{H}_{1(t)}$ is random in time, it will be averaged out over time. This leads to the vanishing of the first term on the right-hand side of equation (2.93). Moreover, it is useful to change the integral variable: let $t' = t - \tau$ and note that $\int_0^t f(t') dt' = -\int_t^0 f(t-\tau) d\tau = \int_0^t f(t-\tau) d\tau$. Then,

$$\begin{aligned} \frac{d\tilde{\rho}(t)}{dt} &= - \int_0^t \langle [\hat{H}_{1(t)}, [\hat{H}_{1(t-\tau)}, \tilde{\rho}(t-\tau)]] \rangle d(t-\tau) \\ &= - \int_0^t \langle [\hat{H}_{1(t)}, [\hat{H}_{1(t-\tau)}, \tilde{\rho}(t-\tau)]] \rangle d\tau, \end{aligned} \quad (2.94)$$

where $\langle \dots \rangle$ denotes the ensemble average over τ . The correlation between $\hat{H}_{1(t)}$ and $\hat{H}_{1(t-\tau)}$ is supposed to drop so fast that the evolution of the density matrix in the interaction picture can be ignored in the correlation period [99]. Therefore, it is appropriate to keep $\tilde{\rho}(t-\tau)$ as $\tilde{\rho}(t)$ and extend the integral to infinity:

$$\frac{d\tilde{\rho}(t)}{dt} = - \int_0^\infty \langle [\hat{H}_{1(t)}, [\hat{H}_{1(t-\tau)}, \tilde{\rho}(t)]] \rangle d\tau. \quad (2.95)$$

Now, transferring back to the Schrödinger picture, we find:

$$\begin{aligned} \frac{d\rho(t)}{dt} &= \frac{d}{dt} (e^{-i\hat{H}_0 t} \tilde{\rho}(t) e^{i\hat{H}_0 t}) \\ &= -i[\hat{H}_0, \rho(t)] - e^{-i\hat{H}_0 t} \left(\int_0^\infty \langle [\hat{H}_{1(t)}, [\hat{H}_{1(t-\tau)}, \tilde{\rho}(t)]] \rangle d\tau \right) e^{i\hat{H}_0 t} \\ &= -i[\hat{H}_0, \rho(t)] - \int_0^\infty \langle [\hat{H}_{1(t)}, [e^{-i\hat{H}_0 \tau} \hat{H}_{1(t-\tau)} e^{i\hat{H}_0 \tau}, \rho(t)]] \rangle d\tau, \end{aligned} \quad (2.96)$$

which is known as the Redfield master equation consisting of two terms: the first governs the coherent dynamics of the system, and the second represents the stochastic motions that cause relaxation.

2.5.2 Relaxation superoperator

The second term in equation (2.96) is often represented as a relaxation superoperator $\hat{\hat{R}}$ in Liouville space.

Liouville space

Operators defined on an n -dimensional Hilbert space, are themselves elements of an n^2 -dimensional vector space known as Liouville space (also known as operator

space). A density matrix, ρ , in Hilbert space is row-wise flattened as a vector denoted by σ in Liouville space, e.g. for a 2×2 density matrix in Hilbert space, it will be a 4×1 vector in Liouville space:

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \Leftrightarrow \sigma = \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix}. \quad (2.97)$$

An operator in Hilbert space $\hat{A}$ needs to be transformed to its superoperator $\hat{\hat{A}}$ in Liouville space. For instance, the commutation operation in Hilbert space $[\hat{A}, \rho] = \hat{A}\rho - \rho\hat{A}$ is represented as the commutation superoperator $\hat{\hat{A}}$ acting on σ in Liouville space, where $\hat{\hat{A}} = \hat{A} \otimes \hat{1} - \hat{1} \otimes \hat{A}^\intercal$. Moreover, $[\hat{B}, [\hat{A}, \rho]] \Leftrightarrow \hat{\hat{B}}\hat{\hat{A}}\sigma$.

2.5.3 Details of $\hat{\hat{R}}$

Letting $\hat{T}_{(\tau)} = e^{-i\hat{H}_0\tau}$, equation (2.96) can be written in Liouville space,

$$\frac{d\sigma_{(t)}}{dt} = -i\hat{\hat{H}}_0 \sigma_{(t)} - \int_0^\infty \langle \hat{\hat{H}}_{1(t)} \hat{\hat{W}}_{(t-\tau)} \rangle d\tau \sigma_{(t)}, \quad (2.98)$$

where $\hat{\hat{H}}_0 = \hat{H}_0 \otimes \hat{1} - \hat{1} \otimes \hat{H}_0^\intercal$, $\hat{\hat{H}}_{1(t)} = \hat{H}_{1(t)} \otimes \hat{1} - \hat{1} \otimes \hat{H}_{1(t)}^\intercal$, and $\hat{\hat{W}}_{(t-\tau)} = \hat{W}_{(t-\tau)} \otimes \hat{1} - \hat{1} \otimes \hat{W}_{(t-\tau)}^\intercal$ with $\hat{W}_{(t-\tau)} = \hat{T}_{(\tau)} \hat{H}_{(t-\tau)} \hat{T}_{(\tau)}^\dagger$. We find that $\hat{\hat{W}}_{(t-\tau)}$ can equivalently be written,

$$\hat{\hat{W}}_{(t-\tau)} = \hat{\hat{T}}_{(\tau)} \hat{\hat{H}}_{1(t-\tau)} \hat{\hat{T}}_{(\tau)}^\dagger, \quad (2.99)$$

where $\hat{\hat{T}}_{(\tau)} = \hat{T}_{(\tau)} \otimes \hat{T}_{(\tau)}^*$ (“*” denotes the complex conjugate). *Proof:* for a unitary operator $\hat{U}$ with its superoperator $\hat{\hat{U}} = \hat{U} \otimes \hat{U}^*$, and a Hermitian operator $\hat{A}$ with its commutation superoperator $\hat{\hat{A}}$, we have:

$$\begin{aligned} \hat{\hat{U}} \hat{\hat{A}} \hat{\hat{U}}^\dagger &= (\hat{U} \otimes \hat{U}^*)(\hat{A} \otimes \hat{1} - \hat{1} \otimes \hat{A}^\intercal)(\hat{U} \otimes \hat{U}^*)^\dagger \\ &= (\hat{U} \hat{A} \otimes \hat{U}^* - \hat{U} \otimes \hat{U}^* \hat{A}^\intercal)(\hat{U}^\dagger \otimes \hat{U}^\intercal) \\ &= (\hat{U} \hat{A} \hat{U}^\dagger) \otimes (\hat{U}^* \hat{U}^\intercal) - (\hat{U} \hat{U}^\dagger) \otimes (\hat{U}^* \hat{A}^\intercal \hat{U}^\intercal) \\ &= (\hat{U} \hat{A} \hat{U}^\dagger) \otimes \hat{1} - \hat{1} \otimes (\hat{U} \hat{A} \hat{U}^\dagger)^\intercal. \end{aligned} \quad (2.100)$$

Now the representation of a relaxation superoperator is obtained:

$$\hat{R} = \int_0^\infty \langle \hat{H}_{1(t)} \hat{T}_{(\tau)} \hat{H}_{1(t-\tau)} \hat{T}_{(\tau)}^\dagger \rangle d\tau. \quad (2.101)$$

Write $\hat{H}_{1(t)}$, $\hat{H}_{1(t-\tau)}$ and $\hat{T}_{(\tau)}$ in the eigenbasis of $\hat{H}_0$. Then, $\hat{T}_{(\tau)}$ ($\hat{T}_{(\tau)}^*$) is diagonal with the j -th diagonal element $\hat{T}_{(\tau)j} = e^{-i\omega_j\tau}$ ($\hat{T}_{(\tau)j}^* = e^{i\omega_j\tau}$), where ω_j denotes an eigenvalue of $\hat{H}_0$. Thus, $\hat{T}_{(\tau)}$ ($\hat{T}_{(\tau)}^\dagger$) is also diagonal with the p -th diagonal element $\hat{T}_{(\tau)p} = e^{-i(\omega_j-\omega_k)\tau} = e^{-i\epsilon_p\tau}$ ($\hat{T}_{(\tau)p}^\dagger = e^{i(\omega_j-\omega_k)\tau} = e^{i\epsilon_p\tau}$), where $p = (j-1)n + k$ (note that n is the dimension of $\hat{T}_{(\tau)}$, so that $j, k \leq n$ and $p \leq n^2$). Now, the matrix element of $\hat{R}$ is obtained,

$$\begin{aligned} \hat{R}_{mn} &= \sum_p \int_0^\infty \langle \hat{H}_{1(t)mp} \hat{T}_{(\tau)pp} \hat{H}_{1(t-\tau)pn} \hat{T}_{(\tau)n}^\dagger \rangle d\tau \\ &= \sum_p \int_0^\infty \langle \hat{H}_{1(t)mp} \hat{H}_{1(t-\tau)pn} \rangle e^{-i(\epsilon_p-\epsilon_n)\tau} d\tau, \end{aligned} \quad (2.102)$$

where $\langle \hat{H}_{1(t)mp} \hat{H}_{1(t-\tau)pn} \rangle$ are the correlation functions of the stochastic process.

The correlation functions often have the form of exponential decay,

$$\langle \hat{H}_{1(t)mp} \hat{H}_{1(t-\tau)pn} \rangle = \langle \hat{H}_{1(t)mp} \hat{H}_{1(t)pn} \rangle e^{-\frac{\tau}{\tau_c}}, \quad (2.103)$$

where τ_c is the correlation time. Thus,

$$\begin{aligned} \hat{R}_{mq} &= \sum_p \int_0^\infty \langle \hat{H}_{1(t)mp} \hat{H}_{1(t)pn} \rangle e^{-i(\epsilon_p-\epsilon_n)\tau} e^{-\frac{\tau}{\tau_c}} d\tau \\ &= \sum_p \langle \hat{H}_{1(t)mp} \hat{H}_{1(t)pn} \rangle \mathcal{J}_{(\epsilon_{pn})}, \end{aligned} \quad (2.104)$$

where $\epsilon_{pn} = \epsilon_p - \epsilon_n$ and

$$\mathcal{J}_{(\epsilon_{pn})} = \frac{\tau_c}{\tau_c^2 \epsilon_{pn}^2 + 1} - i \frac{\epsilon_{pn} \tau_c^2}{\tau_c^2 \epsilon_{pn}^2 + 1} \approx \frac{\tau_c}{\tau_c^2 \epsilon_{pn}^2 + 1} \quad (2.105)$$

is the spectral density. It is usually appropriate to ignore the imaginary parts of $\mathcal{J}_{(\epsilon_{pn})}$ which are the small dynamic frequency shifts [101]. In the extreme narrowing limit (i.e. $\tau_c^2 \epsilon_{pn}^2 \ll 1$) where the stochastic processes (e.g. the molecular rotations) take place on a timescale much shorter than the energy gaps of the

unperturbed Hamiltonian, the spectral density can be further simplified to be the correlation time, $\mathcal{J}_{(\epsilon_{pn})} = \tau_c$, and the relaxation operator,

$$\hat{R} = \tau_c \langle \hat{H}_{1(t)} \hat{H}_{1(t)} \rangle. \quad (2.106)$$

Little is known about these relaxation pathways in cryptochromes, though there are computational studies [63, 64] in which some stochastic processes, such as the librational motions of the radicals, which modulate the hyperfine interactions, were taken into account. According to Ref. [63], the directional sensitivity of the FAD-based radical pair to the external weak magnetic field is surprisingly immune to the spin relaxation, if the $\text{FAD}^{\bullet-}$ radical is paired with a radical devoid of magnetic nuclei. In Ref. [64], it is promising that the directional sensitivity and its angular precision can possibly be preserved even under the fast relaxation caused by the less restricted motion of the tryptophan radical than the flavin radical. In Chapter 5, we show that specific spin relaxation mechanism accounts for the time-dependence of the magnetic field effects repeatedly detected by experiments. Furthermore, such spin relaxation, much faster than chemical reactions, might not destroy the directional sensitivity of the magnetoreceptor in cryptochromes.

Chapter 3

On the anisotropic weak magnetic field effect and the reference-probe model

An external magnetic field can alter the yields of the reaction products of a radical pair through its modulation of the interconversion of the electronic singlet and triplet states [97]. The modulation must be sensitive to the direction of the magnetic field and not just its intensity, such that the radical pair can potentially act as a compass. In radical pairs, there exist anisotropic intra-radical magnetic interactions, mainly the hyperfine interactions in organic radicals, e.g. the two nitrogens N5 and N10 in the $\text{FAD}^{\bullet-}$ radical [102] (Appendix A). Thus, the applied weak magnetic field perturbs the spin system anisotropically depending on its direction relative to the quantization axis set by the internal interactions, such that the modulation of the singlet-triplet interconversion is anisotropic. This is illustrated by the time-dependent singlet fraction for the radical pair in Figure 3.1. In the presence of the weak magnetic field, the fast oscillations caused by the hyperfine interaction are still visible but are superimposed on the slower modulation from the weak Zeeman interaction. It is clear to see that the details of the oscillations change with respect to the orientation of the external magnetic field, allowing the yields of the reaction products to show anisotropy. This anisotropy is considered as the source of the navigational information in a radical pair based magnetoreceptor.

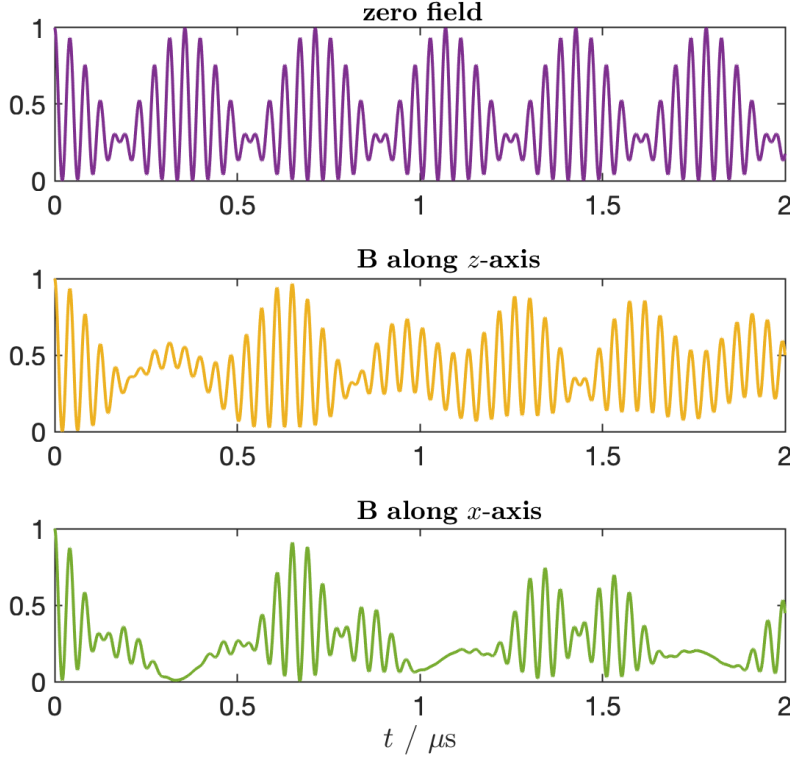


Figure 3.1: The time-dependent singlet probability with or without a $50 \mu\text{T}$ external magnetic field (along the z -axis or x -axis). The spin system is a simple one-proton radical pair with $A_{zz} = 1.7 \text{ mT}$, $A_{xx} = A_{yy} = -0.1 \text{ mT}$. Chemical reactions and spin relaxation have not been included in the calculation.

The effect of a magnetic field is often quantitatively characterized by the difference between the singlet yields of a radical pair with and without the presence of the field, which is denoted by $\Delta\Phi_{S(\omega_0)}^{\mathbf{n}}$ [102],

$$\Delta\Phi_{S(\omega_0)}^{\mathbf{n}} = \Phi_{S(\omega_0)}^{\mathbf{n}} - \Phi_{S(0)}, \quad (3.1)$$

where ω_0 denotes the strength of the external magnetic field and the unit vector $\mathbf{n}$ characterizes the orientation of the field. The difference between the maximum and the minimum of $\Delta\Phi_{S(\omega_0)}^{\mathbf{n}}$ (equivalently $\Phi_{S(\omega_0)}^{\mathbf{n}}$ given that $\Phi_{S(0)}$ in equation (3.1) is obviously not dependent on the direction of the magnetic field) with respect to $\mathbf{n}$, which is denoted by $\Delta\Phi_{S(\omega_0)} = \max(\Delta\Phi_{S(\omega_0)}^{\mathbf{n}}) - \min(\Delta\Phi_{S(\omega_0)}^{\mathbf{n}}) = \max(\Phi_{S(\omega_0)}^{\mathbf{n}}) - \min(\Phi_{S(\omega_0)}^{\mathbf{n}})$, is often used to quantify the anisotropic response to

the magnetic field direction [102].

Earth’s magnetic field is $\sim 50 \mu\text{T}$, which is small relative to the typical hyperfine interactions, around several hundred microtesla [102]. According to equation (2.84) [54],

$$\Phi_{\text{S}} = \frac{1}{Z} \sum_{m,n} |P_{mn}^{\text{S}}|^2 f_{(\omega_{mn})}, \quad (3.2)$$

the singlet yield is closely related to the Lorentzian function $f_{(\omega_{mn})} = \frac{k^2}{k^2 + \omega_{mn}^2}$. If a quantum frequency ω_{mn} is far larger than the recombination rate constant k , $f_{(\omega_{mn})}$ vanishes. An external weak magnetic field is not able to perturb such ω_{mn} to avoid the vanished $f_{(\omega_{mn})}$. Therefore, the weak magnetic field possibly has appreciable effects on $f_{(\omega_{mn})}$ when ω_{mn} is zero, i.e. the degenerate subspaces of the spin Hamiltonian in the absence of the external field. This is the so-called low field effect [54]. Moreover, the small components of axially symmetric hyperfine interactions can be comparable to the external magnetic field, i.e. $A_{xx} = A_{yy} \sim \omega_0$. Thus, there exist nearly degenerate subspaces where weak magnetic effects can arise. To acquire more details of how a weak magnetic field affects these (nearly) degenerate subspaces so as to reveal most clearly the principles of the anisotropic magnetic field effect, we apply degenerate perturbation theory to the investigation of the anisotropic magnetic field perturbation to a very simple radical pair spin system (i.e. a one-proton radical pair) as the “toy model”. Furthermore, the fundamental of the conceptual “reference-probe” model will be realized after the degenerate perturbation analysis.

3.1 Degenerate perturbation treatment

We consider the case of a radical pair with a single spin-1/2 nucleus, e.g., a proton. The hyperfine tensor is set highly axial: $A_{xx} = A_{yy} = \varepsilon$, $A_{zz} = a$ and $\varepsilon \ll a$. The unperturbed spin Hamiltonian of radical 1 is denoted by $\hat{H}_0$ with the matrix

3.1. Degenerate perturbation treatment

representation written as:

$$\hat{H}_0 = \hat{\mathbf{S}}_1 \cdot \mathbf{A} \cdot \hat{\mathbf{I}} = \begin{pmatrix} \frac{a}{4} & 0 & 0 & 0 \\ 0 & -\frac{a}{4} & \frac{\varepsilon}{2} & 0 \\ 0 & \frac{\varepsilon}{2} & -\frac{a}{4} & 0 \\ 0 & 0 & 0 & \frac{a}{4} \end{pmatrix}. \quad (3.3)$$

The perturbative Zeeman interaction Hamiltonian of the electron in radical 1 is denoted by $\delta\hat{H} = \boldsymbol{\omega}_0 \cdot \hat{\mathbf{S}}_1$, where $\boldsymbol{\omega}_0 = -\gamma_e \mathbf{B}_0$. In radical 2 where no nuclear spin is included, the Hamiltonian describing the Zeeman interaction of the electron with the external magnetic field is denoted by $\hat{H}_2 = \boldsymbol{\omega}_0 \cdot \hat{\mathbf{S}}_2$.

3.1.1 Magnetic field along z -axis

We first investigate the case where the magnetic field is along the z -axis. Then, the matrix representation of $\delta\hat{H}$ is:

$$\delta\hat{H} = \begin{pmatrix} \frac{\omega_0}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_0}{2} & 0 & 0 \\ 0 & 0 & -\frac{\omega_0}{2} & 0 \\ 0 & 0 & 0 & -\frac{\omega_0}{2} \end{pmatrix}. \quad (3.4)$$

The four eigenstates of $\hat{H}_0$ are:

$$|1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, |3^{(0)}\rangle = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, |4^{(0)}\rangle = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, \quad (3.5)$$

with energy eigenvalues,

$$\omega_1^{(0)} = \frac{a}{4}, \omega_2^{(0)} = \frac{a}{4}, \omega_3^{(0)} = -\frac{a}{4} + \frac{\varepsilon}{2}, \omega_4^{(0)} = -\frac{a}{4} - \frac{\varepsilon}{2}, \quad (3.6)$$

where the superscript denotes the perturbative order. We find that $|1^{(0)}\rangle$ and $|2^{(0)}\rangle$ are degenerate (i.e. they form a degenerate subspace denoted by $\mathcal{H}^{12}$). Fortunately, $\delta\hat{H}$ has already been diagonal in $\mathcal{H}^{12}$. Then, the first order perturbations to ω_1 and ω_2 are $\omega_1^{(1)} = \omega_0/2$ and $\omega_2^{(1)} = -\omega_0/2$. Furthermore, $\delta\hat{H}$ does not link $|1^{(0)}\rangle$ and $|2^{(0)}\rangle$ with $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$ (e.g. $\langle 3^{(0)}|\delta\hat{H}|1^{(0)}\rangle = 0$), such that

higher orders of perturbations to energy eigenvalues in $\mathcal{H}^{12}$, $\mathcal{O}(\omega_1^{(2)})$ and $\mathcal{O}(\omega_2^{(2)})$, vanish. As for the non-degenerate $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$, the energy gap between the two unperturbed eigenstates is ε which can realistically be comparable to ω_0 at the order of 10 μT . Therefore, $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$ construct a nearly degenerate subspace, $\mathcal{H}^{34}$. According to Ref. [103], the first-order perturbations to energy in $\mathcal{H}^{34}$ are zero:

$$\omega_3^{(1)} = \langle 3^{(0)} | \delta \hat{H} | 3^{(0)} \rangle = 0, \quad \omega_4^{(1)} = \langle 4^{(0)} | \delta \hat{H} | 4^{(0)} \rangle = 0. \quad (3.7)$$

Nevertheless, as $\delta \hat{H}$ is not diagonal in $\mathcal{H}^{34}$, the second-order perturbations, $\omega_3^{(2)}$ and $\omega_4^{(2)}$, are

$$\omega_3^{(2)} = - \sum_{k \neq 3} \frac{|\delta \hat{H}_{k3}|^2}{\omega_k^{(0)} - \omega_3^{(0)}} = \frac{\omega_0^2}{4\varepsilon}, \quad \omega_4^{(2)} = - \sum_{k \neq 4} \frac{|\delta \hat{H}_{k4}|^2}{\omega_k^{(0)} - \omega_4^{(0)}} = -\frac{\omega_0^2}{4\varepsilon}, \quad (3.8)$$

where $\delta \hat{H}_{mn} = \langle m | \delta \hat{H} | n \rangle$. Note that we have assumed that $|\varepsilon| \gg \omega_0$ here. The first order perturbations to the state kets in $\mathcal{H}^{34}$ are [103]

$$\begin{aligned} |3^{(1)}\rangle &= - \sum_{k \neq 3} \frac{\delta \hat{H}_{k3}}{\omega_k^{(0)} - \omega_3^{(0)}} |k^{(0)}\rangle = \frac{\omega_0}{2\varepsilon} |4^{(0)}\rangle, \\ |4^{(1)}\rangle &= - \sum_{k \neq 4} \frac{\delta \hat{H}_{k4}}{\omega_k^{(0)} - \omega_4^{(0)}} |k^{(0)}\rangle = -\frac{\omega_0}{2\varepsilon} |3^{(0)}\rangle. \end{aligned} \quad (3.9)$$

Thus, the perturbed energy eigenstates for radical 1 are obtained with renormalization:

$$\begin{aligned} |1'\rangle &= |1^{(0)}\rangle, \quad |2'\rangle = |2^{(0)}\rangle, \\ |3'\rangle &= \frac{2\varepsilon}{\sqrt{4\varepsilon^2 + \omega_0^2}} |3^{(0)}\rangle + \frac{\omega_0}{\sqrt{4\varepsilon^2 + \omega_0^2}} |4^{(0)}\rangle, \\ |4'\rangle &= \frac{2\varepsilon}{\sqrt{4\varepsilon^2 + \omega_0^2}} |4^{(0)}\rangle - \frac{\omega_0}{\sqrt{4\varepsilon^2 + \omega_0^2}} |3^{(0)}\rangle, \end{aligned} \quad (3.10)$$

with the energy eigenvalues,

$$\begin{aligned} \omega_1' &= \frac{a}{4} + \frac{\omega_0}{2}, \quad \omega_2' = \frac{a}{4} - \frac{\omega_0}{2}, \\ \omega_3' &= -\frac{a}{4} + \frac{\varepsilon}{2} + \frac{\omega_0^2}{4\varepsilon}, \quad \omega_4' = -\frac{a}{4} - \frac{\varepsilon}{2} - \frac{\omega_0^2}{4\varepsilon}. \end{aligned} \quad (3.11)$$

3.1. Degenerate perturbation treatment

As for radical 2, the application of the weak magnetic field breaks the degeneracy of the two-component spin eigenkets,

$$|z_+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |z_-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (3.12)$$

with eigenvalues $\omega_+ = \omega_0/2$ and $\omega_- = -\omega_0/2$. They construct the spin space of the radical 2, denoted by $\mathcal{H}_{r2}$. The inter-electron interactions have been ignored. Then, the eight eigenstates for the radical pair are the direct products of the eigenstates for radical 1 and for radical 2 (e.g. $|1'; z_+\rangle = |1'\rangle \otimes |z_+\rangle$).

For the one-proton radical pair (the nuclear spin dimension, $Z = 2$), the singlet projection operator can be written as:

$$\begin{aligned} \hat{P}^S = & \frac{1}{2} |\uparrow\downarrow\alpha\rangle\langle\uparrow\downarrow\alpha| + \frac{1}{2} |\downarrow\uparrow\alpha\rangle\langle\downarrow\uparrow\alpha| - \frac{1}{2} |\uparrow\downarrow\alpha\rangle\langle\downarrow\uparrow\alpha| - \frac{1}{2} |\downarrow\uparrow\alpha\rangle\langle\uparrow\downarrow\alpha| \\ & + \frac{1}{2} |\uparrow\downarrow\beta\rangle\langle\uparrow\downarrow\beta| + \frac{1}{2} |\downarrow\uparrow\beta\rangle\langle\downarrow\uparrow\beta| - \frac{1}{2} |\uparrow\downarrow\beta\rangle\langle\downarrow\uparrow\beta| - \frac{1}{2} |\downarrow\uparrow\beta\rangle\langle\uparrow\downarrow\beta|, \end{aligned} \quad (3.13)$$

where the arrows “ $\uparrow$ ” and “ $\downarrow$ ” denote the electron spin states and “ α ” and “ β ” denote the nuclear spin states. The coherences refer to $\hat{P}^S$ sandwiched between two different eigenstates for the radical pair, denoted by $\hat{P}_{p'z_j, q'z_k}^S$:

$$P_{p'z_j, q'z_k}^S = \langle p'; z_j | \hat{P}^S | q'; z_k \rangle, \quad (3.14)$$

where $p, q = 1, 2, 3, 4$ and $j, k = \pm$. We suppose that the coherences connecting $\mathcal{H}^{12}$ and $\mathcal{H}^{34}$, such as $P_{1'z_+, 3'z_-}^S$, can appropriately be excluded from discussion when focusing on $\Delta\Phi_{S(\omega_0)}^Z$, as the energy gap ω will be too large ($\sim a/2 \gg k, \omega_0$) such that $f_{(\omega)} \ll 1$, leading to a negligible contribution to $\Delta\Phi_{S(\omega_0)}^Z$. This will be checked concretely later by comparing the perturbation and the exact simulation results. Thus, the discussion will be about $\mathcal{H}^{12}$ and $\mathcal{H}^{34}$ separately.

The four eigenstates for the radical pair in $\mathcal{H}^{12} \otimes \mathcal{H}_{r2}$ are represented, using

“ $\uparrow$ ”, “ $\downarrow$ ”, “ α ” and “ β ”, as:

$$\begin{aligned} |1'; z_+\rangle &= |\uparrow\uparrow \alpha\rangle, \quad |1'; z_-\rangle = |\uparrow\downarrow \alpha\rangle, \\ |2'; z_+\rangle &= |\downarrow\uparrow \beta\rangle, \quad |2'; z_-\rangle = |\downarrow\downarrow \beta\rangle. \end{aligned} \quad (3.15)$$

Recalling the representation of $\hat{P}^S$ in equation (3.13), the coherence of the electronic singlet state is non-zero only if both of the eigenstates connected by such coherence have anti-parallel electronic spin elements and describe the same nuclear spin state. Thus, according to the representation of the four eigenstates in equation (3.15), the coherences within $\mathcal{H}^{12} \otimes \mathcal{H}_{r2}$ are all zero:

$$P_{1'z_+, 2'z_+}^S = P_{1'z_+, 2'z_-}^S = P_{1'z_-, 2'z_+}^S = P_{1'z_-, 2'z_-}^S = 0. \quad (3.16)$$

Thus, according to equation (3.2), no contribution from $\mathcal{H}^{12}$ to $\Delta\Phi_{S(\omega_0)}^z$ is expected.

The four eigenstates for the radical pair in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ are represented as:

$$\begin{aligned} |3'; z_+\rangle &\stackrel{\text{eff}}{=} \frac{1}{\sqrt{2}} \frac{2\varepsilon - \omega_0}{\sqrt{4\varepsilon^2 + \omega_0^2}} |\downarrow\uparrow \alpha\rangle, \quad |3'; z_-\rangle \stackrel{\text{eff}}{=} \frac{1}{\sqrt{2}} \frac{2\varepsilon + \omega_0}{\sqrt{4\varepsilon^2 + \omega_0^2}} |\uparrow\downarrow \beta\rangle, \\ |4'; z_+\rangle &\stackrel{\text{eff}}{=} -\frac{1}{\sqrt{2}} \frac{2\varepsilon + \omega_0}{\sqrt{4\varepsilon^2 + \omega_0^2}} |\downarrow\uparrow \alpha\rangle, \quad |4'; z_-\rangle \stackrel{\text{eff}}{=} \frac{1}{\sqrt{2}} \frac{2\varepsilon - \omega_0}{\sqrt{4\varepsilon^2 + \omega_0^2}} |\uparrow\downarrow \beta\rangle, \end{aligned} \quad (3.17)$$

where “eff” indicates that only the anti-parallel electron spin elements are preserved. Then, the coherences in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ under the perturbation of the weak magnetic field are:

$$\begin{aligned} P_{3'z_+, 3'z_-}^S &= P_{4'z_+, 4'z_-}^S = 0, \\ P_{3'z_+, 4'z_-}^S &= P_{3'z_-, 4'z_+}^S = 0, \\ P_{3'z_+, 4'z_+}^S &= -\frac{1}{4} \times \frac{4\varepsilon^2 - \omega_0^2}{4\varepsilon^2 + \omega_0^2}, \quad P_{3'z_-, 4'z_-}^S = \frac{1}{4} \times \frac{4\varepsilon^2 - \omega_0^2}{4\varepsilon^2 + \omega_0^2}, \end{aligned} \quad (3.18)$$

whereas in the absence of the field, $P_{3^{(0)}z_+, 4^{(0)}z_+}^S = -\frac{1}{4}$ and $P_{3^{(0)}z_-, 4^{(0)}z_-}^S = \frac{1}{4}$. Therefore, the contribution to $\Delta\Phi_{S(\omega_0)}^z$ as a result of the perturbations to the coherences and the corresponding energy gaps within $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ (called the

3.1. Degenerate perturbation treatment

coherence contribution denoted by Δ_{coh}^{34}) is, according to equation (3.2):

$$\begin{aligned}
\Delta_{\text{coh}}^{34} &= \frac{1}{2} \times (|\hat{P}_{3'z_+, 4'z_+}^S|^2 f_{(\omega'_3 - \omega'_4)} + |\hat{P}_{4'z_+, 3'z_+}^S|^2 f_{(\omega'_4 - \omega'_3)}) \\
&\quad + |\hat{P}_{3'z_-, 4'z_-}^S|^2 f_{(\omega'_3 - \omega'_4)} + |\hat{P}_{4'z_-, 3'z_-}^S|^2 f_{(\omega'_4 - \omega'_3)}) \\
&\quad - \frac{1}{2} \times (|\hat{P}_{3^{(0)}z_+, 4^{(0)}z_+}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})} + |\hat{P}_{4^{(0)}z_+, 3^{(0)}z_+}^S|^2 f_{(\omega_4^{(0)} - \omega_3^{(0)})} \dots \\
&\quad + |\hat{P}_{3^{(0)}z_-, 4^{(0)}z_-}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})} + |\hat{P}_{4^{(0)}z_-, 3^{(0)}z_-}^S|^2 f_{(\omega_4^{(0)} - \omega_3^{(0)})}) \\
&= \frac{1}{2} \times 4 \times \left(\frac{1}{4} \times \frac{4\varepsilon^2 - \omega_0^2}{4\varepsilon^2 + \omega_0^2}\right)^2 \times \frac{k^2}{k^2 + (\varepsilon + \frac{\omega_0^2}{2\varepsilon})^2} - \frac{1}{2} \times 4 \times \left(\frac{1}{4}\right)^2 \times \frac{k^2}{k^2 + \varepsilon^2} \\
&= \frac{1}{8} \times \left(\left(\frac{4\varepsilon^2 - \omega_0^2}{4\varepsilon^2 + \omega_0^2}\right)^2 \times \frac{k^2}{k^2 + (\varepsilon + \frac{\omega_0^2}{2\varepsilon})^2} - \frac{k^2}{k^2 + \varepsilon^2}\right). \tag{3.19}
\end{aligned}$$

Let $\varepsilon = -100 \mu\text{T}$, $\omega_0 = 50 \mu\text{T}$ and $k = 1 \mu\text{s}^{-1}$, so that $\Delta_{\text{coh}}^{34} = -0.000155 \approx 0$. However, this deviates far from the exact simulation result with $\Delta\Phi_{\text{S}(50\mu\text{T})}^{\mathbf{z}} = 0.025$ (Figure 3.2), meaning that there must be contributions other than from the coherences. The previous study of a radical pair with an isotropic hyperfine interaction [54] omits the discussion of the change in the eigenvectors by the weak magnetic field. This is because in that case $\varepsilon = a \gg \omega_0$, the perturbations of ω_0 to $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$ are appropriately ignored. As for a radical pair with a highly axial hyperfine interaction, ε can be comparable to ω_0 . Thus, the change in $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$ by ω_0 could be significant, thereby making an appreciable difference to the populations of the two eigenstates in $\hat{P}^S$. The populations here are represented as $P_{j'z_m}^S = \langle j'; z_m | \hat{P}^S | j'; z_m \rangle$. In $\mathcal{H}^{34} \otimes \mathcal{H}_{\text{r2}}$,

$$P_{3'z_+}^S = P_{4'z_-}^S = \frac{1}{4} \times \frac{(2\varepsilon - \omega_0)^2}{4\varepsilon^2 + \omega_0^2}, \quad P_{3'z_-}^S = P_{4'z_+}^S = \frac{1}{4} \times \frac{(2\varepsilon + \omega_0)^2}{4\varepsilon^2 + \omega_0^2}. \tag{3.20}$$

In the absence of the external magnetic field, $P_{3^{(0)}z_+}^S = P_{3^{(0)}z_-}^S = P_{4^{(0)}z_+}^S = P_{4^{(0)}z_-}^S = 1/4$. It is significant to note that, according to equation (3.2), the singlet yield is also related to the squares of the eigenstate populations. The contribution to $\Delta\Phi_{\text{S}(\omega_0)}^{\mathbf{z}}$ from the eigenstate populations altered by the weak magnetic field, called

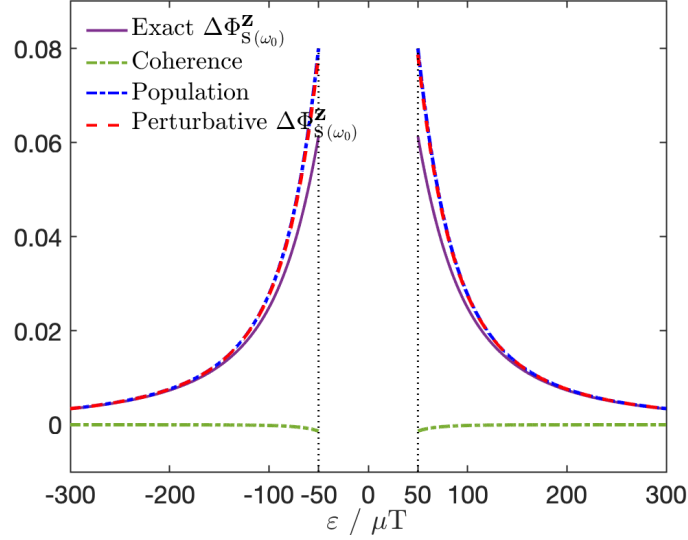


Figure 3.2: One-proton radical pair with $A_{zz} = 1.7$ mT, $k = 10^6$ s $^{-1}$ and $\omega_0 = 50$ μ T. The exact and the perturbative $\Delta\Phi_{S(\omega_0)}^z$ are illustrated as a function of $A_{xx} = A_{yy} = \varepsilon$ in the range $50 < |\varepsilon| < 300$ μ T. The coherence and the population contributions are shown separately. Perturbative $\Delta\Phi_{S(\omega_0)}^z = \Delta_{\text{coh}}^{34} + \Delta_{\text{pop}}^{34}$.

the population contribution denoted by Δ_{pop}^{34} , is obtained as:

$$\begin{aligned} \Delta_{\text{pop}}^{34} &= \frac{1}{2} \sum_{\substack{j=3,4 \\ m=\pm}} (|P_{j'z_m}^S|^2 - |P_{j^{(0)}z_m}^S|^2) \\ &= \frac{1}{16} \times \frac{(2\varepsilon + \omega_0)^4 + (2\varepsilon - \omega_0)^4}{(4\varepsilon^2 + \omega_0^2)^2} - \frac{1}{8} \\ &= \frac{2\varepsilon^2\omega_0^2}{(4\varepsilon^2 + \omega_0^2)^2}. \end{aligned} \quad (3.21)$$

Then, total $\Delta\Phi_{S(\omega_0)}^z$ is:

$$\begin{aligned} \Delta\Phi_{S(\omega_0)}^z &= \Delta_{\text{coh}}^{34} + \Delta_{\text{pop}}^{34} \\ &= \frac{1}{8} \times \left(\left(\frac{4\varepsilon^2 - \omega_0^2}{4\varepsilon^2 + \omega_0^2} \right)^2 \times \frac{k^2}{k^2 + \left(\varepsilon + \frac{\omega_0^2}{2\varepsilon} \right)^2} - \frac{k^2}{k^2 + \varepsilon^2} \right) + \frac{2\varepsilon^2\omega_0^2}{(4\varepsilon^2 + \omega_0^2)^2}. \end{aligned} \quad (3.22)$$

Assigning ε and ω_0 as before, $\Delta_{\text{pop}}^{34} = 0.0277$, so that $\Delta\Phi_{S(50\mu\text{T})}^z = \Delta_{\text{coh}}^{34} + \Delta_{\text{pop}}^{34} \approx 0.0275$, satisfactorily close to the exact numerical simulation result 0.025. In Figure 3.2, the exact numerical simulation (purple solid traces) and the perturbation treatment (red dashed traces) are compared for $50 < |\varepsilon| < 300$ μ T. The larger the $|\varepsilon|$ is than ω_0 , the more satisfactory the perturbation method becomes. ε in this

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range gives rise to the negligible coherence contribution, i.e. $\Delta_{\text{coh}}^{34} \approx 0$. The population contribution, originating in the change in the zero-field eigenstructure of the degenerate subspaces, accounts for the major change in the reaction yield. Moreover, $\Delta\Phi_{\text{S}(\omega_0)}^{\mathbf{z}} > 0$ is shown by equation (3.21) with the positive Δ_{pop}^{34} . This means that the singlet-triplet interconversion for the singlet-born radical pair is actually hindered by the magnetic field along the z -axis so that the singlet yield is increased.

When $|\varepsilon| < \omega_0$, we have to reconstruct $\delta\hat{H}$ and $\hat{H}_0$ (taking ε as the perturbation and ω_0 as part of the unperturbed $\hat{H}_0$):

$$\delta\hat{H} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\varepsilon}{2} & 0 \\ 0 & \frac{\varepsilon}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \hat{H}_0 = \begin{pmatrix} \frac{a+2\omega_0}{4} & 0 & 0 & 0 \\ 0 & \frac{-a+2\omega_0}{4} & 0 & 0 \\ 0 & 0 & \frac{-a-2\omega_0}{4} & 0 \\ 0 & 0 & 0 & \frac{a-2\omega_0}{4} \end{pmatrix}. \quad (3.23)$$

$\mathcal{H}^{12}$ is not affected, but $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$ are different:

$$|3^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |4^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ -1 \\ 0 \end{pmatrix}, \quad (3.24)$$

with energy eigenvalues,

$$\omega_3^{(0)} = -\frac{a}{4} + \frac{\omega_0}{2}, \quad \omega_4^{(0)} = -\frac{a}{4} - \frac{\omega_0}{2}. \quad (3.25)$$

Applying the perturbation theory, we find that the first order perturbations to the energy $\omega_3^{(1)}$ and $\omega_4^{(1)}$ are still zero. The second order perturbations $\omega_3^{(2)}$ and $\omega_4^{(2)}$ are:

$$\omega_3^{(2)} = -\sum_{k \neq 3} \frac{|\delta\hat{H}_{k3}|^2}{\omega_k^{(0)} - \omega_3^{(0)}} = \frac{\varepsilon^2}{4\omega_0}, \quad \omega_4^{(2)} = -\sum_{k \neq 4} \frac{|\delta\hat{H}_{k4}|^2}{\omega_k^{(0)} - \omega_4^{(0)}} = -\frac{\varepsilon^2}{4\omega_0}. \quad (3.26)$$

The first-order perturbations to the eigenstates, $|3^{(1)}\rangle$ and $|4^{(1)}\rangle$, are:

$$\begin{aligned} |3^{(1)}\rangle &= -\sum_{k \neq 3} \frac{\delta\hat{H}_{k3}}{\omega_k^{(0)} - \omega_3^{(0)}} |k^{(0)}\rangle = -\frac{\varepsilon}{2\omega_0} |4^{(0)}\rangle, \\ |4^{(1)}\rangle &= -\sum_{k \neq 4} \frac{\delta\hat{H}_{k4}}{\omega_k^{(0)} - \omega_4^{(0)}} |k^{(0)}\rangle = \frac{\varepsilon}{2\omega_0} |3^{(0)}\rangle. \end{aligned} \quad (3.27)$$

Then, the perturbed eigenstates $|3'\rangle$ and $|4'\rangle$ are obtained through renormalization:

$$\begin{aligned} |3'\rangle &= \frac{2\omega_0}{\sqrt{4\omega_0^2 + \varepsilon^2}} |3^{(0)}\rangle - \frac{\varepsilon}{\sqrt{4\omega_0^2 + \varepsilon^2}} |4^{(0)}\rangle, \\ |4'\rangle &= \frac{2\omega_0}{\sqrt{4\omega_0^2 + \varepsilon^2}} |4^{(0)}\rangle + \frac{\varepsilon}{\sqrt{4\omega_0^2 + \varepsilon^2}} |3^{(0)}\rangle. \end{aligned} \quad (3.28)$$

Combining this with the expression for the perturbed $|3'\rangle$ and $|4'\rangle$ when $|\varepsilon| > \omega_0$ in equation (3.9), we find that the weak magnetic field's reform of the eigenbasis of $\mathcal{H}^{34}$ can be seen as a rotation from $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$ in equation (3.5) towards those in equation (3.24) with respect to the strength of ε . The four eigenstates in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ are:

$$\begin{aligned} |3'; z_+\rangle &\stackrel{\text{eff}}{=} \frac{\varepsilon}{\sqrt{4\omega_0^2 + \varepsilon^2}} |\downarrow\uparrow\alpha\rangle, \quad |3'; z_-\rangle \stackrel{\text{eff}}{=} \frac{2\omega_0}{\sqrt{4\omega_0^2 + \varepsilon^2}} |\uparrow\downarrow\beta\rangle, \\ |4'; z_+\rangle &\stackrel{\text{eff}}{=} -\frac{2\omega_0}{\sqrt{4\omega_0^2 + \varepsilon^2}} |\downarrow\uparrow\alpha\rangle, \quad |4'; z_-\rangle \stackrel{\text{eff}}{=} \frac{\varepsilon}{\sqrt{4\omega_0^2 + \varepsilon^2}} |\uparrow\downarrow\beta\rangle. \end{aligned} \quad (3.29)$$

Thus, the coherences are:

$$\begin{aligned} \hat{P}_{3'z_+, 3'z_-}^S &= \hat{P}_{4'z_+, 4'z_-}^S = \hat{P}_{3'z_+, 4'z_-}^S = \hat{P}_{3'z_-, 4'z_+}^S = 0, \\ \hat{P}_{3'z_+, 4'z_+}^S &= -\frac{\varepsilon\omega_0}{4\omega_0^2 + \varepsilon_0^2}, \quad \hat{P}_{3'z_-, 4'z_-}^S = \frac{\varepsilon\omega_0}{4\omega_0^2 + \varepsilon_0^2}. \end{aligned} \quad (3.30)$$

The coherence contribution to $\Delta\Phi_{S(\omega_0)}^{\mathbf{z}}$ is obtained as:

$$\begin{aligned} \Delta_{\text{coh}}^{34} &= \frac{1}{2} \times (|\hat{P}_{3'z_+, 4'z_+}^S|^2 f_{(\omega'_3 - \omega'_4)} + |\hat{P}_{4'z_+, 3'z_+}^S|^2 f_{(\omega'_4 - \omega'_3)} \dots \\ &\quad + |\hat{P}_{3'z_-, 4'z_-}^S|^2 f_{(\omega'_3 - \omega'_4)} + |\hat{P}_{4'z_-, 3'z_-}^S|^2 f_{(\omega'_4 - \omega'_3)}) \dots \\ &\quad - \frac{1}{2} \times (|\hat{P}_{3^{(0)}z_+, 4^{(0)}z_+}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})} + |\hat{P}_{4^{(0)}z_+, 3^{(0)}z_+}^S|^2 f_{(\omega_4^{(0)} - \omega_3^{(0)})} \dots \\ &\quad + |\hat{P}_{3^{(0)}z_-, 4^{(0)}z_-}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})} + |\hat{P}_{4^{(0)}z_-, 3^{(0)}z_-}^S|^2 f_{(\omega_4^{(0)} - \omega_3^{(0)})}) \\ &= \frac{1}{2} \times 4 \times \left(\frac{\varepsilon\omega_0}{4\omega_0^2 + \varepsilon^2}\right)^2 \times \frac{k^2}{k^2 + (\omega_0 + \frac{\varepsilon^2}{2\omega_0})^2} - \frac{1}{2} \times 4 \times \left(\frac{1}{4}\right)^2 \times \frac{k^2}{k^2 + \varepsilon^2} \\ &= \frac{2\varepsilon^2\omega_0^2}{(4\omega_0^2 + \varepsilon^2)^2} \times \frac{k^2}{k^2 + (\omega_0 + \frac{\varepsilon^2}{2\omega_0})^2} - \frac{1}{8} \times \frac{k^2}{k^2 + \varepsilon^2}. \end{aligned} \quad (3.31)$$

The coherence contribution is always negative, shown by the dash-dotted green line in Figure 3.3. Note that $k = 1 \mu\text{s}^{-1}$ is equivalent to $\sim 5 \mu\text{T}$ in the $f_{(\omega)}$ function.

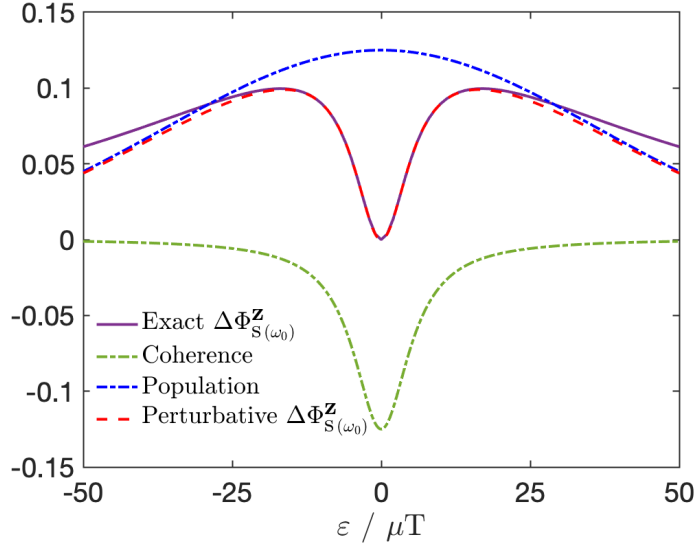


Figure 3.3: One-proton radical pair with $A_{zz} = 1.7$ mT, $k = 10^6$ s $^{-1}$ and $\omega_0 = 50$ μ T. The exact and the perturbative $\Delta\Phi_{S(\omega_0)}^Z$ are illustrated as a function of $A_{xx} = A_{yy} = \varepsilon$ in the range $|\varepsilon| < 50$ μ T. The coherence and the population contributions are shown separately. Perturbative $\Delta\Phi_{S(\omega_0)}^Z = \Delta_{\text{coh}}^{34} + \Delta_{\text{pop}}^{34}$.

Then, $|\varepsilon| \gtrsim 5$ gives rise to a negligible coherence contribution. While $|\varepsilon|$ is becoming smaller than 5 μ T, $\frac{k^2}{k^2 + \varepsilon^2}$ starts to be significant whereas $\frac{k^2}{k^2 + (\omega_0 + \frac{\varepsilon^2}{2\omega_0})^2} \approx 0$, so that $\Delta_{\text{coh}}^{34} \approx -\frac{1}{8} \times \frac{k^2}{k^2 + \varepsilon^2}$. The populations of the eigenstates in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ are:

$$\hat{P}_{3'z_+}^S = \hat{P}_{4'z_-}^S = \frac{1}{2} \times \frac{\varepsilon^2}{4\omega_0^2 + \varepsilon^2}, \quad \hat{P}_{3'z_-}^S = \hat{P}_{4'z_+}^S = \frac{1}{2} \times \frac{4\omega_0^2}{4\omega_0^2 + \varepsilon^2}, \quad (3.32)$$

Thus, the population contribution to $\Delta\Phi_{S(\omega_0)}^Z$ is:

$$\begin{aligned} \Delta_{\text{pop}}^{34} &= \frac{1}{2} \sum_{\substack{j=3,4 \\ m=\pm}} (|\hat{P}_{j'z_m}^S|^2 - |\hat{P}_{j^{(0)}z_m}^S|^2) \\ &= \frac{1}{4} \times \frac{16\omega_0^4 + \varepsilon^4}{(4\omega_0^2 + \varepsilon^2)^2} - \frac{1}{8} \\ &= \frac{1}{8} \times \frac{(4\omega_0^2 - \varepsilon^2)^2}{(4\omega_0^2 + \varepsilon^2)^2}, \end{aligned} \quad (3.33)$$

which is shown by the dash-dot blue line in Figure 3.3. As $|\varepsilon|$ drops to zero, Δ_{pop}^{34}

steadily climbs to its maximum value $1/8$. Now, we will have $\Delta\Phi_{S(\omega_0)}^z$:

$$\begin{aligned}\Delta\Phi_{S(\omega_0)}^z &= \Delta_{\text{coh}}^{34} + \Delta_{\text{pop}}^{34} \\ &= \frac{2\varepsilon^2\omega_0^2}{(4\omega_0^2 + \varepsilon^2)^2} \times \frac{k^2}{k^2 + (\omega_0 + \frac{\varepsilon^2}{2\omega_0})^2} - \frac{1}{8} \times \frac{k^2}{k^2 + \varepsilon^2} + \frac{1}{8} \times \frac{(4\omega_0^2 - \varepsilon^2)^2}{(4\omega_0^2 + \varepsilon^2)^2} \\ &\approx \frac{1}{8} \times \frac{(4\omega_0^2 - \varepsilon^2)^2}{(4\omega_0^2 + \varepsilon^2)^2} - \frac{1}{8} \times \frac{k^2}{k^2 + \varepsilon^2},\end{aligned}\tag{3.34}$$

which is shown by the red dashed line in Figure 3.3. The smaller $|\varepsilon|$ is relative to ω_0 , the better the perturbation treatment agrees with the exact numerical simulation. As $|\varepsilon|$ gets smaller than $15 \mu\text{T}$, the negative coherence contribution and positive population contribution start to cancel each other until $\Delta\Phi_{S(\omega_0)}^z = 0$ when $|\varepsilon| = 0$.

Singlet-triplet interconversion

To obtain a physical understanding of the perturbative results in equations (3.22) and (3.34), we need to investigate their relation to the spin dynamics of the radical pair, i.e. the singlet-triplet interconversion. The yields of the four spin selective reaction products, denoted by $\Phi_{S(\omega_0)}^z$ for S, $\Phi_{0(\omega_0)}^z$ for T_0 , $\Phi_{+(\omega_0)}^z$ for T_+ and $\Phi_{-(\omega_0)}^z$ for T_- , as a function of ε with and without the external $50 \mu\text{T}$ magnetic field are illustrated in Figure 3.4(a). One can clearly see that $\Phi_{S(\omega_0)}^z = \Phi_{0(\omega_0)}^z$ and $\Phi_{+(\omega_0)}^z = \Phi_{-(\omega_0)}^z$. The interconversion between S and T_0 is dominated by the high quantum frequency characterized by $A_{zz} = a$ connecting the two subspaces $\mathcal{H}^{12}$ and $\mathcal{H}^{34}$, which is immune from the weak external magnetic field. It is the S- $T_{\pm}$ and the T_0 - $T_{\pm}$ interconversions induced by ε that are possibly affected by the weak magnetic field through its change in the (nearly) degenerate subspaces and its modulation of the energy gaps. Figure 3.4(a) reveals that the application of the magnetic field along z -axis hinders the S- $T_{\pm}$ and T_0 - $T_{\pm}$ interconversions for the singlet-born radical pair, so that the S and T_0 yields increase whereas the T_+ and T_- yields decrease. Moreover, the increase in the S and T_0 yields is equal to the de-

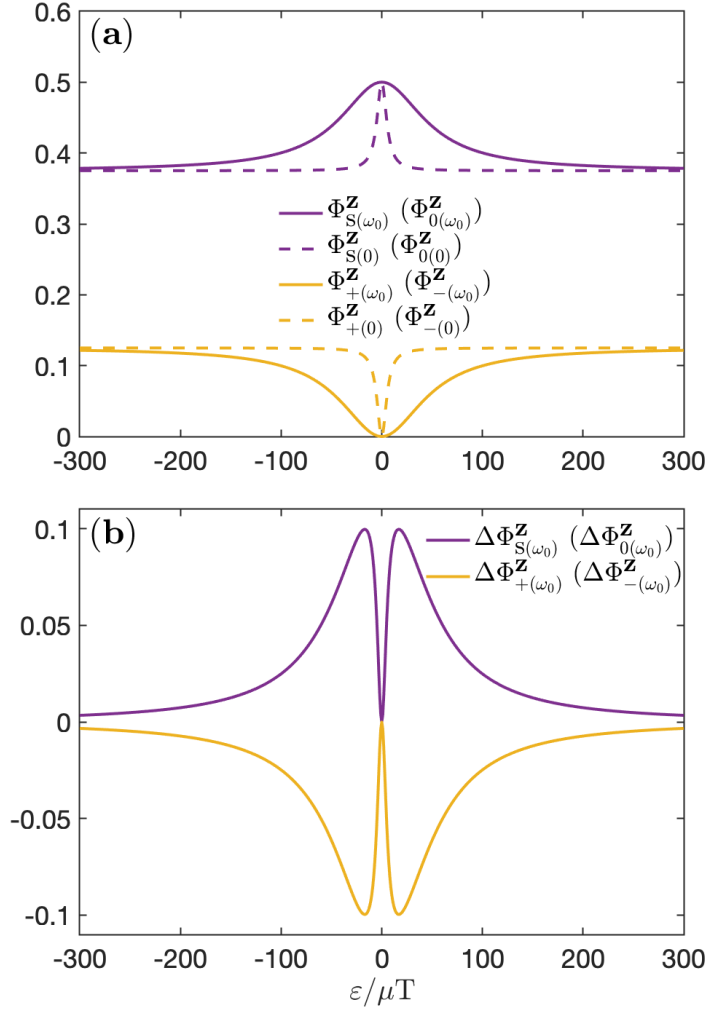


Figure 3.4: One-proton radical pair with $A_{zz} = 1.7$ mT, $k = 10^6$ s $^{-1}$ and $B = 50$ μT . (a) The exact simulation of the yields of the reaction products are illustrated as a function of $A_{xx} = A_{yy} = \varepsilon$ in the range $0 < |\varepsilon| < 300$ μT , with and without the external magnetic field. (b) The difference in the yields caused by the field, $\Delta\Phi^{\mathbf{Z}}_{j(\omega_0)} = \Phi^{\mathbf{Z}}_{j(\omega_0)} - \Phi^{\mathbf{Z}}_{j(0)}$ where $j = \text{S}, 0, +$ and $-$.

crease of the T_+ and T_- yields (i.e. $\Delta\Phi^{\mathbf{Z}}_{\text{S}(\omega_0)} = \Delta\Phi^{\mathbf{Z}}_{0(\omega_0)} = -\Delta\Phi^{\mathbf{Z}}_{+(\omega_0)} = -\Delta\Phi^{\mathbf{Z}}_{-(\omega_0)}$), which is clearly seen in Figure 3.4(b). Based on the perturbation analysis, the effect of the weak magnetic field along the z -axis originates in $\mathcal{H}^{34} \otimes \mathcal{H}_{\text{r}2}$. Thus, we only concentrate on the time-dependent S probability in this subspace, $\text{P}^{\text{S}}_{34(t)}$, which is illustrated in Figure 3.5 where the simulations are for three values of ε , -100 , -15 and -5 μT . Note that the time-dependent T_0 probability in $\mathcal{H}^{34} \otimes \mathcal{H}_{\text{r}2}$, $\text{P}^{\text{T}_0}_{34(t)}$, is identical to $\text{P}^{\text{S}}_{34(t)}$. Detailed discussions will be given with respect to the

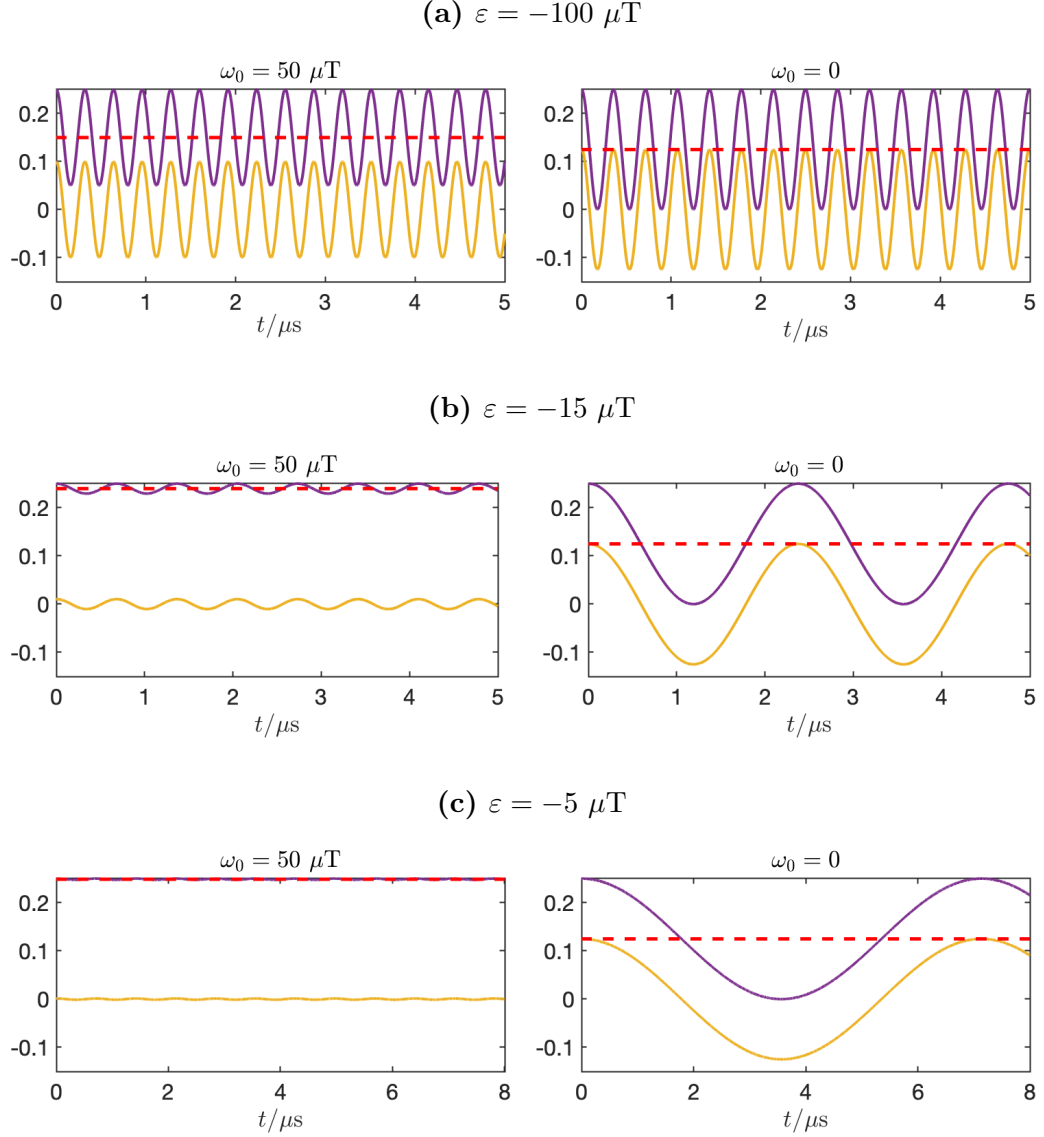


Figure 3.5: One-proton radical pair with $A_{zz} = 1.7 \text{ mT}$ and $B = 50 \mu\text{T}$. $\varepsilon = -100, -15$, and $-5 \mu\text{T}$ in (a), (b) and (c) respectively. No chemical reaction is included. The time-dependent S (T_0) probability in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ is shown by the solid purple traces, the coherence dynamics, $c_{(\omega_0, t)}$, is illustrated by the solid orange traces, and the summation of the squared populations of the eigenstates, $p_{(\omega_0)}$, is shown by the dashed red traces. The solid purple = the solid orange + the dashed red.

ranges of $|\varepsilon|$ relative to ω_0 and k :

- (1) $|\varepsilon| > \omega_0$, represented by $\varepsilon = -100 \mu\text{T}$ in Figure 3.5(a): The application of the weak magnetic field slightly obstructs the S- $T_{\pm}$ and the T_0 - $T_{\pm}$ interconversions.

3.1. Degenerate perturbation treatment

The amplitude of the oscillation of $P_{34(t)}^S$ ($P_{34(t)}^{T_0}$) decreases because of the field, shown by the solid purple line which is viewed as a combination of the coherence dynamics $c_{(\omega_0, t)}$ (orange solid line), and the time-independent $p_{(\omega_0)}$ (red dashed line) describing the populations of the eigenstates in the projection operators. $c_{(\omega_0, t)}$ and $p_{(\omega_0)}$ are represented as:

$$\begin{aligned} c_{(\omega_0, t)} &= \sum_{m \neq n} P_{nm}^{S(T_0)} \rho_{(0)mn} e^{-i(\omega_m - \omega_n)t} = \frac{1}{2} \sum_{m \neq n} P_{nm}^{S(T_0)} P_{mn}^S e^{-i(\omega_m - \omega_n)t}, \\ p_{(\omega_0)} &= \sum_{m=n} P_{nm}^{S(T_0)} \rho_{(0)mn} = \frac{1}{2} \sum_{m=n} P_{nm}^{S(T_0)} P_{mn}^S, \end{aligned} \quad (3.35)$$

where $P_{nm}^{S(T_0)} = \langle n | \hat{P}^{S(T_0)} | m \rangle$, $|m(n)\rangle$ denotes an eigenstate in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ with eigenvalue $\omega_{m(n)}$, and $\rho_{(0)} = \hat{P}^S/2$. $c_{(\omega_0, t)}$ will be averaged out for $\omega_0 = 0$ or $50 \mu\text{T}$ when calculating the singlet yield, as the frequency of the oscillating $c_{(\omega_0, t)}$ is larger than the reaction rate constant, $k = 1 \mu\text{s}^{-1}$. Thus, no appreciable coherence contribution is expected when $|\varepsilon| > \omega_0$. Then, the increase of the singlet yield by the magnetic field is attributed to the $p_{(\omega_0)}$ shown by the red dashed traces in Figure 3.5(a). This originates in the small change, induced by the weak magnetic field, in the eigenbasis of the nearly degenerate subspace $\mathcal{H}^{34}$, i.e. from equation (3.5) to equation (3.10).

(2) $|\varepsilon| < \omega_0$, represented by $\varepsilon = -15 \mu\text{T}$ in Figure 3.5(b): The weak magnetic field tremendously hinders the S - $T_{\pm}$ and the T_0 - $T_{\pm}$ interconversions - only a small fraction of $S(T_0)$ is allowed to interconvert with $T_{\pm}$. Now, $p_{(\omega_0 = 50 \mu\text{T})}$ nearly arrives at its maximum value of $1/4$, thereby resulting in a population contribution $\Delta_{\text{pop}}^{34} \sim 1/8$, obtained according to equation (3.34). $c_{(\omega_0 = 50 \mu\text{T}, t)}$ still oscillates at a frequency larger than k and its amplitude becomes small as a result of the application of the field, so that $c_{(\omega_0 = 50 \mu\text{T}, t)}$ can be ignored in the calculation of singlet yield. On the other hand, $c_{(\omega_0 = 0, t)}$ oscillates at a frequency ($\sim 0.4 \mu\text{s}^{-1}$) smaller than k with a amplitude equal to $1/8$. Therefore, the negative coherence

contribution $\Delta_{\text{coh}}^{34} \propto (c_{(\omega_0=50 \mu\text{T}, t)} - c_{(\omega_0=0, t)})$ starts to be non-negligible as $|\varepsilon|$ becomes smaller than ω_0 .

(3) $|\varepsilon| \lesssim 5 \mu\text{T}$ shown in Figure 3.5(c): In the absence of the field, ε produces very slow conversion from $S(T_0)$ to $T_{\pm}$ during the lifetime of the radical pair. $c_{(\omega_0=0, t)}$ oscillates with a long period, so that its integral over time will not be averaged out, giving a significant $f_{(|\varepsilon| < k)}$. Therefore, the negative Δ_{coh}^{34} becomes significant to cancel the positive Δ_{pop}^{34} , which is embodied in equation (3.34).

3.1.2 Magnetic field along the x -axis

The orientation of weak magnetic field along the x -axis gives a new $\delta\hat{H}$:

$$\delta\hat{H} = \begin{pmatrix} 0 & 0 & \frac{\omega_0}{2} & 0 \\ 0 & 0 & 0 & \frac{\omega_0}{2} \\ \frac{\omega_0}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_0}{2} & 0 & 0 \end{pmatrix}. \quad (3.36)$$

We find that $\delta\hat{H}$ does not break the degeneracy of $|1^{(0)}\rangle$ and $|2^{(0)}\rangle$ to first order. In other words, it is not straightforward to figure out the “good basis” in $\mathcal{H}^{12}$. The degeneracy is then expected to be lifted to second order by $\delta\hat{H}$. We can first express the appropriate $|1^{(0)}\rangle$ and $|2^{(0)}\rangle$ as linear combinations of those in equation (3.4):

$$|1^{(0)}\rangle = a_{11}^{(0)} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} + a_{12}^{(0)} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \quad |2^{(0)}\rangle = a_{21}^{(0)} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} + a_{22}^{(0)} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \quad (3.37)$$

The solutions for these coefficients will be obtained as: $a_{11}^{(0)} = \sqrt{2}/2$, $a_{12}^{(0)} = \sqrt{2}/2$, $a_{21}^{(0)} = \sqrt{2}/2$, $a_{22}^{(0)} = -\sqrt{2}/2$ according to Ref. [103], though the mathematical procedures require some effort. Thus, the four unperturbed eigenstates

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for radical 1 are:

$$|1^{(0)}\rangle = \begin{pmatrix} \frac{\sqrt{2}}{2} \\ 0 \\ 0 \\ \frac{\sqrt{2}}{2} \end{pmatrix}, |2^{(0)}\rangle = \begin{pmatrix} \frac{\sqrt{2}}{2} \\ 0 \\ 0 \\ -\frac{\sqrt{2}}{2} \end{pmatrix}, |3^{(0)}\rangle = \begin{pmatrix} 0 \\ \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} \\ 0 \end{pmatrix}, |4^{(0)}\rangle = \begin{pmatrix} 0 \\ \frac{\sqrt{2}}{2} \\ -\frac{\sqrt{2}}{2} \\ 0 \end{pmatrix}. \quad (3.38)$$

Second-order perturbations to the energy eigenvalues are:

$$\omega_1^{(2)} = \frac{\omega_0^2}{2(a - \varepsilon)}, \omega_2^{(2)} = \frac{\omega_0^2}{2(a + \varepsilon)}, \omega_3^{(2)} = \frac{-\omega_0^2}{2(a - \varepsilon)}, \omega_4^{(2)} = \frac{-\omega_0^2}{2(a + \varepsilon)}, \quad (3.39)$$

and first-order perturbations to the eigenvectors are:

$$\begin{aligned} |1^{(1)}\rangle &= \frac{\omega_0}{a - \varepsilon} |3^{(0)}\rangle, \quad |2^{(1)}\rangle = \frac{\omega_0}{a + \varepsilon} |4^{(0)}\rangle, \\ |3^{(1)}\rangle &= \frac{-\omega_0}{a - \varepsilon} |1^{(0)}\rangle, \quad |4^{(1)}\rangle = \frac{\omega_0}{a + \varepsilon} |2^{(0)}\rangle. \end{aligned} \quad (3.40)$$

We find that all of these perturbations either to the energy eigenvalues or to the eigenstate kets are negligible when $a \gg \omega_0, \varepsilon$. Then one may ask if it is appropriate to ignore these perturbations, as if the weak magnetic field along x -axis was not experienced by radical 1, which will not make a difference to the calculation of the singlet yield. This will be checked stringently through further deduction for the algebraic expression of $\Delta\Phi_{S(\omega_0)}^x$. The perturbed four eigenstates for radical 1 with renormalization are:

$$\begin{aligned} |1'\rangle &= \frac{a_-}{\Omega_-} |1^{(0)}\rangle + \frac{\omega_0}{\Omega_-} |3^{(0)}\rangle, \quad |2'\rangle = \frac{a_+}{\Omega_+} |2^{(0)}\rangle + \frac{\omega_0}{\Omega_+} |4^{(0)}\rangle, \\ |3'\rangle &= \frac{a_-}{\Omega_-} |3^{(0)}\rangle - \frac{\omega_0}{\Omega_-} |1^{(0)}\rangle, \quad |4'\rangle = \frac{a_+}{\Omega_+} |4^{(0)}\rangle + \frac{\omega_0}{\Omega_+} |2^{(0)}\rangle, \end{aligned} \quad (3.41)$$

where $a_{\pm} = a \pm \varepsilon$ and $\Omega_{\pm} = a_{\pm}^2 + \omega_0^2$, with eigenvalues:

$$\begin{aligned} \omega'_1 &= \frac{a}{4} + \frac{\omega_0^2}{2(a - \varepsilon)}, \quad \omega'_2 = \frac{a}{4} + \frac{\omega_0^2}{2(a + \varepsilon)}, \\ \omega'_3 &= -\frac{a}{4} + \frac{\varepsilon}{2} - \frac{\omega_0^2}{2(a - \varepsilon)}, \quad \omega'_4 = -\frac{a}{4} - \frac{\varepsilon}{2} - \frac{\omega_0^2}{2(a + \varepsilon)}. \end{aligned} \quad (3.42)$$

The two eigenstates for radical 2 are:

$$|x_+\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \quad |x_-\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}. \quad (3.43)$$

Then, the perturbed eigenstates for the radical pair in $\mathcal{H}^{12} \otimes \mathcal{H}_{r2}$ are:

$$\begin{aligned}
 |1'; x_+\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(\frac{a_-}{\Omega_-} |\uparrow\downarrow \alpha\rangle + \frac{a_-}{\Omega_-} |\downarrow\uparrow \beta\rangle + \frac{\omega_0}{\Omega_-} |\uparrow\downarrow \beta\rangle + \frac{\omega_0}{\Omega_-} |\downarrow\uparrow \alpha\rangle \right), \\
 |1'; x_-\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(-\frac{a_-}{\Omega_-} |\uparrow\downarrow \alpha\rangle + \frac{a_-}{\Omega_-} |\downarrow\uparrow \beta\rangle - \frac{\omega_0}{\Omega_-} |\uparrow\downarrow \beta\rangle + \frac{\omega_0}{\Omega_-} |\downarrow\uparrow \alpha\rangle \right), \\
 |2'; x_+\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(\frac{a_+}{\Omega_+} |\uparrow\downarrow \alpha\rangle - \frac{a_+}{\Omega_+} |\downarrow\uparrow \beta\rangle + \frac{\omega_0}{\Omega_+} |\uparrow\downarrow \beta\rangle - \frac{\omega_0}{\Omega_+} |\downarrow\uparrow \alpha\rangle \right), \\
 |2'; x_-\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(-\frac{a_+}{\Omega_+} |\uparrow\downarrow \alpha\rangle - \frac{a_+}{\Omega_+} |\downarrow\uparrow \beta\rangle - \frac{\omega_0}{\Omega_+} |\uparrow\downarrow \beta\rangle - \frac{\omega_0}{\Omega_+} |\downarrow\uparrow \alpha\rangle \right)
 \end{aligned} \tag{3.44}$$

Recalling the expression for $\hat{P}^S$ in equation (3.13) gives the coherences in $\mathcal{H}^{12} \otimes \mathcal{H}_{r2}$ under a weak magnetic field:

$$\begin{aligned}
 \hat{P}_{1'x_+, 1'x_-}^S &= \hat{P}_{2'x_+, 2'x_-}^S = 0, \\
 \hat{P}_{1'x_+, 2'x_+}^S &= \hat{P}_{1'x_-, 2'x_-}^S = 0, \\
 \hat{P}_{1'x_+, 2'x_-}^S &= \frac{1}{4} \times \frac{-a_+a_- - \omega_0^2 + (a_+ + a_-)\omega_0}{\Omega_+\Omega_-}, \\
 \hat{P}_{1'x_-, 2'x_+}^S &= \frac{1}{4} \times \frac{-a_+a_- - \omega_0^2 - (a_+ + a_-)\omega_0}{\Omega_+\Omega_-}.
 \end{aligned} \tag{3.45}$$

In the absence of the field, the coherences in $\mathcal{H}^{12} \otimes \mathcal{H}_{r2}$ are:

$$\begin{aligned}
 \hat{P}_{1^{(0)}x_+, 1^{(0)}x_-}^S &= \hat{P}_{2^{(0)}x_+, 2^{(0)}x_-}^S = 0, \\
 \hat{P}_{1^{(0)}x_+, 2^{(0)}x_+}^S &= \hat{P}_{1^{(0)}x_-, 2^{(0)}x_-}^S = 0, \\
 \hat{P}_{1^{(0)}x_+, 2^{(0)}x_-}^S &= \hat{P}_{1^{(0)}x_-, 2^{(0)}x_+}^S = \frac{1}{4}.
 \end{aligned} \tag{3.46}$$

Thus, the coherence contribution to $\Delta\Phi_{S(\omega_0)}^x$ in this subspace is:

$$\begin{aligned}
 \Delta_{\text{coh}}^{12} &= \frac{1}{2} \times \left(|\hat{P}_{1'x_+, 2'x_-}^S|^2 f_{(\omega'_1 - \omega'_2 + \omega_0)} + |\hat{P}_{1'x_-, 2'x_+}^S|^2 f_{(\omega'_1 - \omega'_2 - \omega_0)} \right. \\
 &\quad \left. + |\hat{P}_{2'x_+, 1'x_-}^S|^2 f_{(\omega'_2 - \omega'_1 + \omega_0)} + |\hat{P}_{2'x_-, 1'x_+}^S|^2 f_{(\omega'_2 - \omega'_1 - \omega_0)} \right) \\
 &\quad - \frac{1}{2} \times \left(|\hat{P}_{1^{(0)}x_+, 2^{(0)}x_-}^S|^2 f_{(\omega_1^{(0)} - \omega_2^{(0)})} + |\hat{P}_{1^{(0)}x_-, 2^{(0)}x_+}^S|^2 f_{(\omega_1^{(0)} - \omega_2^{(0)})} \right. \\
 &\quad \left. + |\hat{P}_{2^{(0)}x_+, 1^{(0)}x_-}^S|^2 f_{(\omega_2^{(0)} - \omega_1^{(0)})} + |\hat{P}_{2^{(0)}x_-, 1^{(0)}x_+}^S|^2 f_{(\omega_2^{(0)} - \omega_1^{(0)})} \right) \\
 &= \left(|\hat{P}_{1'x_+, 2'x_-}^S|^2 f_{(\omega'_1 - \omega'_2 + \omega_0)} + |\hat{P}_{1'x_-, 2'x_+}^S|^2 f_{(\omega'_1 - \omega'_2 - \omega_0)} \right) \\
 &\quad - \left(|\hat{P}_{1^{(0)}x_+, 2^{(0)}x_-}^S|^2 f_{(\omega_1^{(0)} - \omega_2^{(0)})} + |\hat{P}_{1^{(0)}x_-, 2^{(0)}x_+}^S|^2 f_{(\omega_1^{(0)} - \omega_2^{(0)})} \right) \\
 &= \left(|\hat{P}_{1'x_+, 2'x_-}^S|^2 f_{(\omega'_1 - \omega'_2 + \omega_0)} + |\hat{P}_{1'x_-, 2'x_+}^S|^2 f_{(\omega'_1 - \omega'_2 - \omega_0)} \right) - \frac{1}{8},
 \end{aligned} \tag{3.47}$$

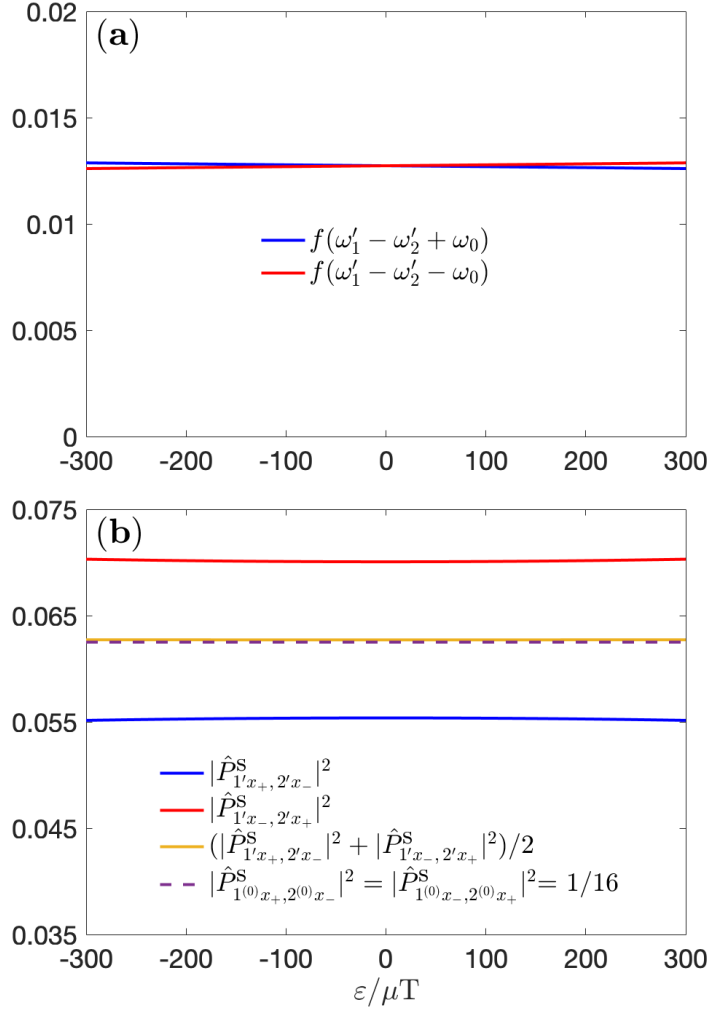


Figure 3.6: One-proton radical pair with $A_{zz} = 1.7$ mT, $\omega_0 = 50$ μT along x -axis and the reaction constant $k = 1$ μs^{-1} . Left: the $f_{(\omega)}$ functions in the coherence contribution with respect to ε . Right: the squared coherences in the coherence contribution with respect to ε with and without the external magnetic field.

where $\omega_1^{(0)} = \omega_2^{(0)}$ so that $f_{(\omega_1^{(0)} - \omega_2^{(0)})} = 1$. $f_{(\omega'_1 - \omega'_2 + \omega_0)}$ and $f_{(\omega'_1 - \omega'_2 - \omega_0)}$ are illustrated in Figure 3.6(a), both of which are satisfactorily close to $f_{(\omega_0)}$. This means that the small energy gap, $\omega'_1 - \omega'_2$, in $\mathcal{H}^{12}$ of radical 1, brought by the external magnetic field, is negligible. It is the Zeeman splitting in radical 2 that contributes to the non-zero Lorentzian function, i.e. $f_{(\omega'_1 - \omega'_2 + \omega_0)} \approx f_{(\omega'_1 - \omega'_2 - \omega_0)} \approx f_{(\omega_0)}$. The calculation of $|\hat{P}^S_{1'x+,2'x-}|^2$ and $|\hat{P}^S_{1'x-,2'x+}|^2$, using equations (3.45) and (3.46), is shown in Figure 3.6(b). We find that the field makes small but non-negligible difference

to $|\hat{P}_{1'x_+, 2'x_-}^S|^2$ and $|\hat{P}_{1'x_-, 2'x_+}^S|^2$. However, it is clear to see that $|\hat{P}_{1'x_+, 2'x_-}^S|^2 + |\hat{P}_{1'x_-, 2'x_+}^S|^2 \approx 2|\hat{P}_{1^{(0)}x_+, 2^{(0)}x_-}^S|^2 = 2|\hat{P}_{1^{(0)}x_-, 2^{(0)}x_+}^S|^2 = 1/8$. In terms of Δ_{coh}^{12} , radical 1 can be considered not to be affected by the weak magnetic field along the x -axis. Thus, remembering equation (3.47), Δ_{coh}^{12} is obtained as

$$\Delta_{\text{coh}}^{12} \approx (|\hat{P}_{1^{(0)}x_+, 2^{(0)}x_-}^S|^2 + |\hat{P}_{1^{(0)}x_-, 2^{(0)}x_+}^S|^2) \times \frac{k^2}{k^2 + \omega_0^2} - \frac{1}{8} = -\frac{1}{8} \times \frac{\omega_0^2}{k^2 + \omega_0^2}. \quad (3.48)$$

The populations of the perturbed eigenstates in $\mathcal{H}^{12} \otimes \mathcal{H}_{r2}$ are:

$$\begin{aligned} P_{1'x_+, 1'x_+}^S &= \frac{1}{4} \times \frac{(a_- - \omega_0)^2}{\Omega_-^2}, & P_{1'x_-, 1'x_-}^S &= \frac{1}{4} \times \frac{(a_- + \omega_0)^2}{\Omega_-^2}, \\ P_{2'x_+, 2'x_+}^S &= \frac{1}{4} \times \frac{(a_+ + \omega_0)^2}{\Omega_+^2}, & P_{2'x_-, 2'x_-}^S &= \frac{1}{4} \times \frac{(a_+ - \omega_0)^2}{\Omega_+^2}. \end{aligned} \quad (3.49)$$

Then, the population contribution to $\Delta\Phi_{S(\omega_0)}^x$ from $\mathcal{H}^{12} \otimes \mathcal{H}_{r2}$ is found to be zero:

$$\begin{aligned} \Delta_{\text{pop}}^{12} &= \frac{1}{2} \sum_{\substack{j=1,2 \\ m=\pm}} (|\hat{P}_{j'x_m, j'x_m}^S|^2 - |\hat{P}_{j^{(0)}x_m, j^{(0)}x_m}^S|^2) \\ &= \frac{1}{2} \times \left(\frac{1}{16} \times \left(2 + \frac{8a_-^2\omega_0^2}{(a_-^2 + \omega_0^2)^2} \right) + \frac{1}{16} \times \left(2 + \frac{8a_+^2\omega_0^2}{(a_+^2 + \omega_0^2)^2} \right) - 4 \times \frac{1}{16} \right) \\ &= \frac{1}{4} \times \left(\frac{a_-^2\omega_0^2}{(a_-^2 + \omega_0^2)^2} + \frac{a_+^2\omega_0^2}{(a_+^2 + \omega_0^2)^2} \right) \\ &\approx 0. \end{aligned} \quad (3.50)$$

In $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$, the perturbed eigenstates are:

$$\begin{aligned} |3'; x_+\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(\frac{a_-}{\Omega_-} |\uparrow\downarrow\beta\rangle + \frac{a_-}{\Omega_-} |\downarrow\uparrow\alpha\rangle - \frac{\omega_0}{\Omega_-} |\uparrow\downarrow\alpha\rangle - \frac{\omega_0}{\Omega_-} |\downarrow\uparrow\beta\rangle \right), \\ |3'; x_-\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(-\frac{a_-}{\Omega_-} |\uparrow\downarrow\beta\rangle + \frac{a_-}{\Omega_-} |\downarrow\uparrow\alpha\rangle + \frac{\omega_0}{\Omega_-} |\uparrow\downarrow\alpha\rangle - \frac{\omega_0}{\Omega_-} |\downarrow\uparrow\beta\rangle \right), \\ |4'; x_+\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(\frac{a_+}{\Omega_+} |\uparrow\downarrow\beta\rangle - \frac{a_+}{\Omega_+} |\downarrow\uparrow\alpha\rangle + \frac{\omega_0}{\Omega_+} |\uparrow\downarrow\alpha\rangle - \frac{\omega_0}{\Omega_+} |\downarrow\uparrow\beta\rangle \right), \\ |4'; x_-\rangle &\stackrel{\text{eff}}{=} \frac{1}{2} \times \left(-\frac{a_+}{\Omega_+} |\uparrow\downarrow\beta\rangle - \frac{a_+}{\Omega_+} |\downarrow\uparrow\alpha\rangle - \frac{\omega_0}{\Omega_+} |\uparrow\downarrow\alpha\rangle - \frac{\omega_0}{\Omega_+} |\downarrow\uparrow\beta\rangle \right). \end{aligned} \quad (3.51)$$

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Then, with the magnetic field, the coherences in $\mathcal{H}^{34} \otimes \hat{H}_{r2}$ are:

$$\begin{aligned}\hat{P}_{3'x_+, 3'x_-}^S &= \hat{P}_{4'x_+, 4'x_-}^S = 0, \\ \hat{P}_{3'x_+, 4'x_+}^S &= \hat{P}_{3'x_-, 4'x_-}^S = 0, \\ \hat{P}_{3'x_+, 4'x_-}^S &= \frac{1}{4} \times \frac{-a_+a_- + \omega_0^2 + (a_- - a_+)\omega_0}{\Omega_+\Omega_-}, \\ \hat{P}_{3'x_-, 4'x_+}^S &= \frac{1}{4} \times \frac{-a_+a_- + \omega_0^2 + (a_+ - a_-)\omega_0}{\Omega_+\Omega_-}.\end{aligned}\tag{3.52}$$

Without the field, they are:

$$\begin{aligned}\hat{P}_{3^{(0)}x_+, 4^{(0)}x_-}^S &= \hat{P}_{2^{(0)}x_+, 2^{(0)}x_-}^S = 0, \\ \hat{P}_{3^{(0)}x_+, 4^{(0)}x_+}^S &= \hat{P}_{3^{(0)}x_-, 4^{(0)}x_-}^S = 0, \\ \hat{P}_{3^{(0)}x_+, 4^{(0)}x_-}^S &= \hat{P}_{3^{(0)}x_-, 4^{(0)}x_+}^S = \frac{1}{4}.\end{aligned}\tag{3.53}$$

Then, the coherence contribution from $\mathcal{H}^{34} \otimes \hat{H}_{r2}$ is:

$$\begin{aligned}\Delta_{\text{coh}}^{34} &= \frac{1}{2} \times (|\hat{P}_{3'x_+, 4'x_-}^S|^2 f_{(\omega'_3 - \omega'_4 + \omega_0)} + |\hat{P}_{3'x_-, 4'x_+}^S|^2 f_{(\omega'_3 - \omega'_4 - \omega_0)} \dots \\ &\quad + |\hat{P}_{4'x_+, 3'x_-}^S|^2 f_{(\omega'_4 - \omega'_3 + \omega_0)} + |\hat{P}_{4'x_-, 3'x_+}^S|^2 f_{(\omega'_4 - \omega'_3 - \omega_0)}) \dots \\ &\quad - \frac{1}{2} \times (|\hat{P}_{3^{(0)}x_+, 4^{(0)}x_-}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})} + |\hat{P}_{3^{(0)}x_-, 4^{(0)}x_+}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})} \dots \\ &\quad + |\hat{P}_{4^{(0)}x_+, 3^{(0)}x_-}^S|^2 f_{(\omega_4^{(0)} - \omega_3^{(0)})} + |\hat{P}_{4^{(0)}x_-, 3^{(0)}x_+}^S|^2 f_{(\omega_4^{(0)} - \omega_3^{(0)})}) \\ &= (|\hat{P}_{3'x_+, 4'x_-}^S|^2 f_{(\omega'_3 - \omega'_4 + \omega_0)} + |\hat{P}_{3'x_-, 4'x_+}^S|^2 f_{(\omega'_3 - \omega'_4 - \omega_0)}) \dots \\ &\quad - (|\hat{P}_{3^{(0)}x_+, 4^{(0)}x_-}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})} + |\hat{P}_{3^{(0)}x_-, 4^{(0)}x_+}^S|^2 f_{(\omega_3^{(0)} - \omega_4^{(0)})}) \\ &= (|\hat{P}_{3'x_+, 4'x_-}^S|^2 f_{(\omega'_3 - \omega'_4 + \omega_0)} + |\hat{P}_{3'x_-, 4'x_+}^S|^2 f_{(\omega'_3 - \omega'_4 - \omega_0)}) - \frac{1}{8} f(\varepsilon).\end{aligned}\tag{3.54}$$

The Lorentzian functions, $f_{(\omega'_3 - \omega'_4 + \omega_0)}$ and $f_{(\omega'_3 - \omega'_4 - \omega_0)}$, are shown in Figure 3.7(a).

$f_{(\omega'_3 - \omega'_4 \pm \omega_0)} \approx f_{(\omega_3^{(0)} - \omega_4^{(0)} \pm \omega_0)} \approx f_{(\varepsilon \pm \omega_0)}$, as according to equation (3.43), $\omega'_3 - \omega'_4 = \varepsilon - \frac{\varepsilon\omega_0^2}{a^2 - \omega_0^2} \approx \varepsilon$ with $a \gg \omega_0$. Thus, the negligible modulation of the energy levels in $\mathcal{H}^{34}$ of radical 1 by the weak magnetic field can be ignored. Δ_{coh}^{34} is discussed with respect to the ranges of ε :

(1) $|\varepsilon| > 100 \mu\text{T}$: the Lorentzian functions are negligible for $\omega_0 = 0$ and $50 \mu\text{T}$, i.e. $f_{(\varepsilon \pm \omega_0)} \approx f_{(\varepsilon)} \approx 0$. Besides, $|\hat{P}_{3'x_+, 4'x_-}^S|^2 + |\hat{P}_{3'x_-, 4'x_+}^S|^2 \approx 2|\hat{P}_{3^{(0)}x_+, 4^{(0)}x_-}^S|^2 =$

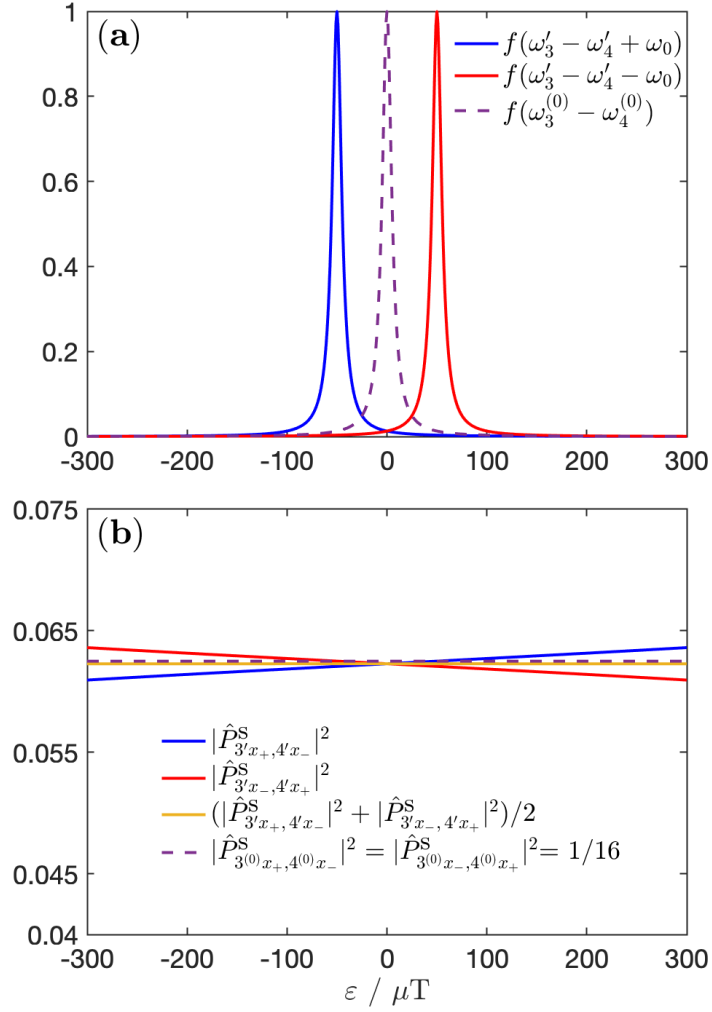


Figure 3.7: Same as Figure 3.6 but in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$.

$2|\hat{P}_{3^{(0)}x_-, 4^{(0)}x_+}^S|^2 = 1/8$, shown by the solid orange line and the dashed purple line Figure 3.7(b). Thus, the coherence contribution from $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ to $\Delta\Phi_{S(\omega_0)}^x$ is zero, $\Delta_{\text{coh}}^{34} \approx 0$.

(2) $|\varepsilon| < 100 \mu\text{T}$: $|\hat{P}_{3'x_+, 4'x_-}^S|^2 \approx |\hat{P}_{3'x_-, 4'x_+}^S|^2 \approx |\hat{P}_{3^{(0)}x_+, 4^{(0)}x_-}^S|^2 = |\hat{P}_{3^{(0)}x_-, 4^{(0)}x_+}^S|^2 = 1/16$, so that it is appropriate to ignore the change in the eigenvectors in $\mathcal{H}^{34}$ of radical 1 by the weak field, i.e. $|3'\rangle = |3^{(0)}\rangle$ and $|4'\rangle = |4^{(0)}\rangle$. Therefore, Δ_{coh}^{34} in

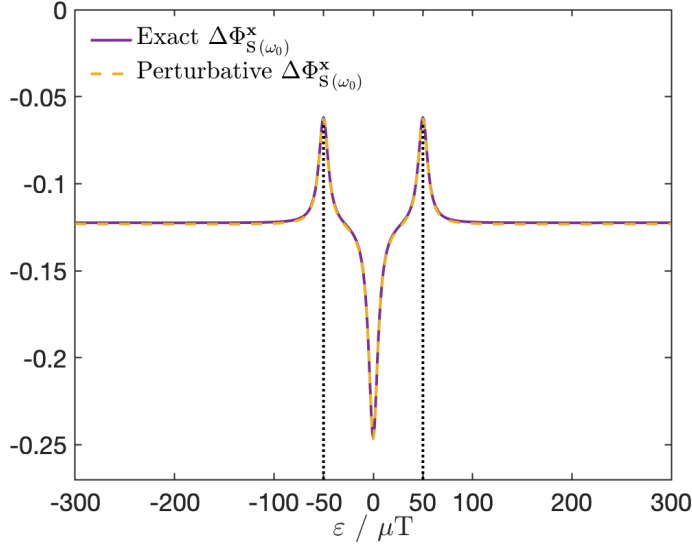


Figure 3.8: One-proton radical pair with $A_{zz} = 1.7$ mT, $k = 10^6$ s $^{-1}$ and $\omega_0 = 50$ μ T. The exact and the perturbative $\Delta\Phi_{S(\omega_0)}^z$ are illustrated as a function of $A_{xx} = A_{yy} = \varepsilon$.

equation (3.54) can be obtained as:

$$\begin{aligned}
\Delta_{\text{coh}}^{34} &= (|\hat{P}_{3'x+, 4'x-}^S|^2 f_{(\omega'_3 - \omega'_4 + \omega_0)} + |\hat{P}_{3'x-, 4'x+}^S|^2 f_{(\omega'_3 - \omega'_4 - \omega_0)}) - \frac{1}{8} f(\varepsilon) \\
&= \frac{1}{16} (f_{(\varepsilon + \omega_0)} + f_{(\varepsilon - \omega_0)}) - \frac{1}{8} f(\varepsilon) \\
&= \frac{1}{16} \times \left(\frac{k^2}{k^2 + (\varepsilon + \omega_0)^2} + \frac{k^2}{k^2 + (\varepsilon - \omega_0)^2} \right) - \frac{1}{8} \times \frac{k^2}{k^2 + \varepsilon^2}.
\end{aligned} \tag{3.55}$$

Specifically, $\varepsilon = \text{either } \omega_0 \text{ or } -\omega_0$ gives $\Delta_{\text{coh}}^{34} \approx \frac{1}{16} \times \frac{\omega_0^2 - k^2}{\omega_0^2 + k^2} > 0$, which makes a positive contribution to $\Delta\Phi_{S(\omega_0)}^x$ indicating a deficiency of the S-T interconversion in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$. However, small A_{xx} and A_{yy} ($|\varepsilon| \ll k$), in the absence of the external field, are unable to cause an efficient S-T interconversion during the radical-pair lifetime. The application of the weak magnetic field along the x -axis greatly promotes the S-T interconversion, thereby decreasing the singlet yield with a negative coherence contribution, $\Delta_{\text{coh}}^{34} = \frac{1}{8} \times \frac{k^2}{k^2 + \omega_0^2} - \frac{1}{8} = -\frac{1}{8} \times \frac{\omega_0^2}{k^2 + \omega_0^2}$.

The populations of the perturbed eigenstates in $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ are:

$$\begin{aligned}
 \hat{P}_{3'x_+, 3'x_+}^S &= \frac{1}{4} \times \frac{(a_- + \omega_0)^2}{\Omega_-^2}, & \hat{P}_{3'x_-, 3'x_-}^S &= \frac{1}{4} \times \frac{(a_- - \omega_0)^2}{\Omega_-^2}, \\
 \hat{P}_{4'x_+, 4'x_+}^S &= \frac{1}{4} \times \frac{(a_+ + \omega_0)^2}{\Omega_+^2}, & \hat{P}_{4'x_-, 4'x_-}^S &= \frac{1}{4} \times \frac{(a_+ - \omega_0)^2}{\Omega_+^2}.
 \end{aligned} \tag{3.56}$$

Thus, the population contribution from $\mathcal{H}^{34} \otimes \mathcal{H}_{r2}$ to $\Delta\Phi_{S(\omega_0)}^x$ is found to be zero:

$$\begin{aligned}
 \Delta_{\text{pop}}^{34} &= \frac{1}{2} \sum_{\substack{j=3,4 \\ m=\pm}} (|\hat{P}_{j'x_m, j'x_m}^S|^2 - |\hat{P}_{j^{(0)}x_m, j^{(0)}x_m}^S|^2) \\
 &= \frac{1}{2} \times \left(\frac{1}{16} \times \left(2 + \frac{8a_-^2\omega_0^2}{(a_-^2 + \omega_0^2)^2} \right) + \frac{1}{16} \times \left(2 + \frac{8a_+^2\omega_0^2}{(a_+^2 + \omega_0^2)^2} \right) - 4 \times \frac{1}{16} \right) \\
 &= \frac{1}{4} \times \left(\frac{a_-^2\omega_0^2}{(a_-^2 + \omega_0^2)^2} + \frac{a_+^2\omega_0^2}{(a_+^2 + \omega_0^2)^2} \right) \\
 &\approx 0.
 \end{aligned} \tag{3.57}$$

Based on the perturbation treatment in the two (nearly) degenerate subspaces (i.e. $\mathcal{H}^{12}$ and $\mathcal{H}^{34}$), $\Delta\Phi_{S(\omega_0)}^x$ entirely originates in the coherence contribution ($\Delta_{\text{pop}}^{12} \approx \Delta_{\text{pop}}^{34} \approx 0$ according to equations (3.50) and (3.57)):

$$\begin{aligned}
 \Delta\Phi_{S(\omega_0)}^x &= \Delta_{\text{coh}}^{12} + \Delta_{\text{coh}}^{34} \\
 &= -\frac{1}{8} \times \frac{\omega_0^2}{k^2 + \omega_0^2} + \frac{1}{16} \times \left(\frac{k^2}{k^2 + (\varepsilon + \omega_0)^2} + \frac{k^2}{k^2 + (\varepsilon - \omega_0)^2} \right) \\
 &\quad - \frac{1}{8} \times \frac{k^2}{k^2 + \varepsilon^2}.
 \end{aligned} \tag{3.58}$$

As is shown in Figure 3.8, the perturbative $\Delta\Phi_{S(\omega_0)}^x$ in equation (3.58) agrees satisfactorily with the exact simulation. Unlike the weak magnetic field along the z -axis that modulates the S-T interconversion mainly through changing the eigenstructure in the (nearly) degenerate subspaces, the weak field along the x -axis is unable to notably change the eigenvectors but can promote the S-T interconversion ($\Delta\Phi_{S(\omega_0)}^x < 0$) for the singlet-born radical pair via its effect on the coherence dynamics. Specifically, the S- T_0 interconversion is not directly influenced by the application of the weak field along the x -axis, but the efficiency of the S- $T_{\pm}$ and T_0 - $T_{\pm}$ interconversions is appreciably increased by the field. In Figure 3.9(a), $\Phi_{S(0)}^x = \Phi_{0(0)}^x$, $\Phi_{S(\omega_0)}^x = \Phi_{0(\omega_0)}^x$, $\Phi_{+(0)}^x = \Phi_{-(0)}^x$, $\Phi_{+(\omega_0)}^x = \Phi_{-(\omega_0)}^x$. In Figure 3.9(b), $\Delta\Phi_{S(\omega_0)}^x = \Delta\Phi_{T_0(\omega_0)}^x = -\Delta\Phi_{T_+(\omega_0)}^x = -\Delta\Phi_{T_-(\omega_0)}^x$.

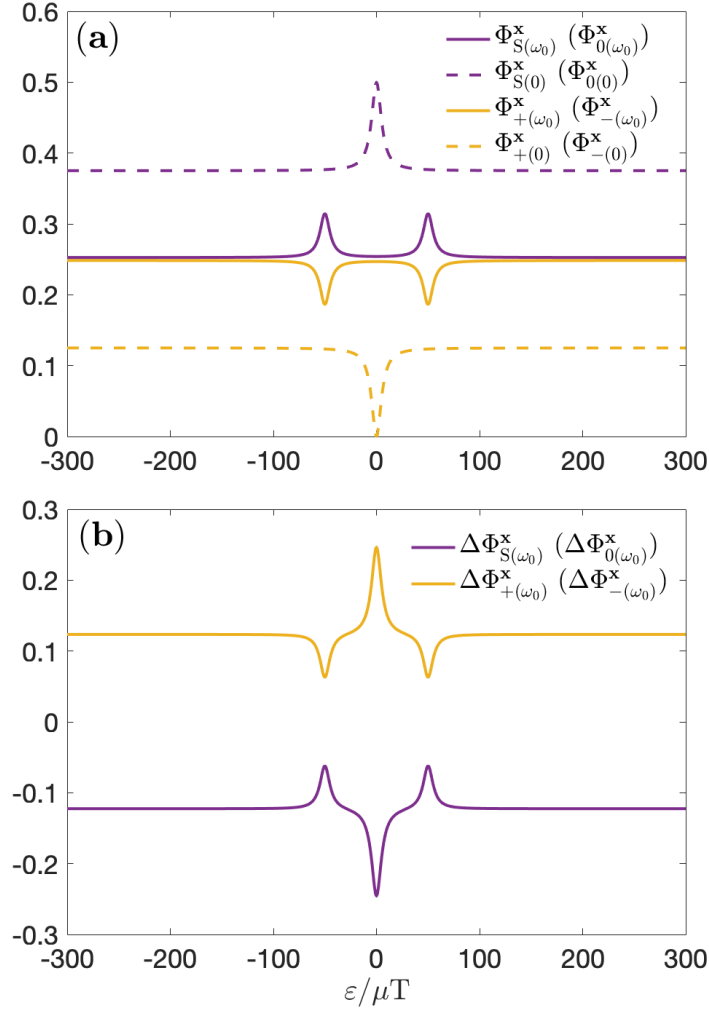


Figure 3.9: One-proton radical pair with $A_{zz} = 1.7$ mT, $k = 10^6$ s $^{-1}$ and $\omega_0 = 50$ μT . (a) The exact simulation of the yields of the reaction products are illustrated as a function of $A_{xx} = A_{yy} = \varepsilon$ in the range $0 < |\varepsilon| < 300$ μT , with and without the external magnetic field. (b) The difference in the yields caused by the field, $\Delta\Phi_{j(\omega_0)}^x = \Phi_{j(\omega_0)}^x - \Phi_{j(0)}^x$ where $j = S, 0, +$ and $-$.

3.1.3 Conclusion

The perturbation treatment of the (nearly) degenerate subspaces in a radical pair successfully characterizes the anisotropic weak magnetic field effect on the product yield of the spin selective reaction. All the analytical $\Delta\Phi_{S(\omega_0)}^n$ (i.e. equation (3.22) for $|\varepsilon| > \omega_0$ and equation (3.34) for $|\varepsilon| < \omega_0$ when the external magnetic field is along z -axis, and equation (3.58) when the external magnetic field is along

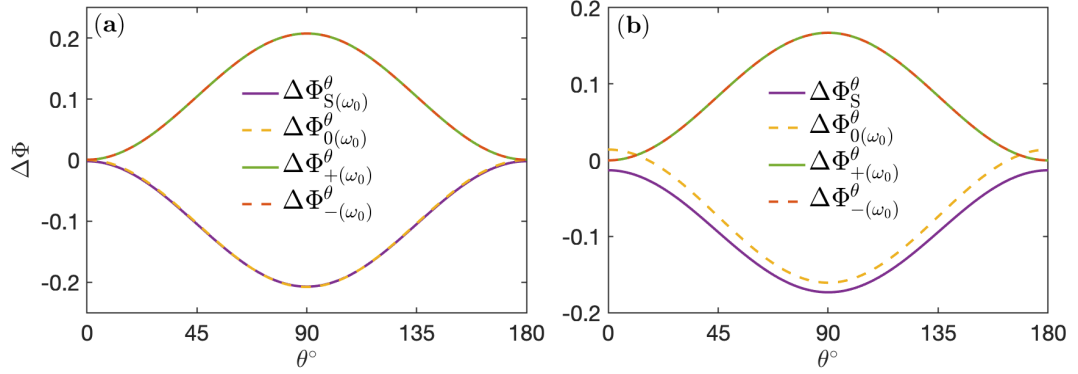


Figure 3.10: $\Delta\Phi_{S(\omega_0)}^\theta$, $\Delta\Phi_{0(\omega_0)}^\theta$, $\Delta\Phi_{+(\omega_0)}^\theta$ and $\Delta\Phi_{-(\omega_0)}^\theta$ as a function of θ for the FAD-Z radical pair. (a) N5 and N10 in the $\text{FAD}^{\bullet-}$ radical. (b) N5, N10, H6 and 3×H8 in the $\text{FAD}^{\bullet-}$ radical.

x -axis) match the exact simulation results satisfactorily (Figures 3.2, 3.3 and 3.8). This verifies that the coherences **between** these subspaces are appropriately ignored because of their negligible contribution to the modulation of the reaction production yield from the weak magnetic field. The eigenvectors in the (nearly) degenerate subspaces could be changed, so that their populations in the radical-pair spin space are re-allocated, as some components of the hyperfine tensors could be comparable to the weak magnetic field. This change in the eigenbasis is anisotropic with respect to the field direction relative to the quantization axis of the hyperfine interactions. At some field orientation, the re-allocation of the eigenstates in the (nearly) degenerate subspaces contributes the major part of the magnetic field effect on the reaction yield. For some specific orientation of the external magnetic field, its disturbance to the eigenstates is negligible, but the extra energy splitting caused by the weak Zeeman interaction remarkably influences the coherence dynamics in the (nearly) degenerate subspaces. Furthermore, unlike a one-proton radical pair with an isotropic hyperfine interaction where the weak magnetic field affects the radical-pair reactions through opening new pathways for S- T_0 interconversion [104] (Appendix B), the anisotropic weak field effect on the one-proton radical pair with an axial hyperfine interaction relies on its modulation

3.2. Reference-probe model

of the S-T_± and T₀-T_± interconversions. This is still true for a radical pair with more hyperfine interactions - the FAD-Z radical pair (no nuclear spin in the Z[•] radical). The change in the S, T₀, T₊ and T₋ yields as a function of the field direction, θ , are calculated,

$$\Delta\Phi_{J(\omega_0)}^\theta = \Phi_{J(\omega_0)}^\theta - \Phi_{J(0)} \quad \text{for } J = S, 0, +, -. \quad (3.59)$$

In Figure 3.10(a), $\Delta\Phi_{S(\omega_0)}^\theta = \Delta\Phi_{0(\omega_0)}^\theta = -\Delta\Phi_{+(\omega_0)}^\theta = -\Delta\Phi_{-(\omega_0)}^\theta$ when only two nitrogens with nearly axial hyperfine interactions are included in the FAD^{•-} radical, meaning that the anisotropic weak low field effect is embodied in the S-T_± and T₀-T_± interconversions. Adding hydrogens, especially the three H8 with isotropic hyperfine interactions, opens a small extra pathway for the S-T₀ interconversion (Figure 3.10(b)). Nevertheless, the response to the direction of the external magnetic field still relies on the field's modulation of the S-T_± and T₀-T_± interconversions, as in Figure 3.10(b), $\Delta\Phi_{S(\omega_0)} \approx \Delta\Phi_{0(\omega_0)} \approx -\Delta\Phi_{+(\omega_0)} = -\Delta\Phi_{-(\omega_0)}$ with the definition:

$$\Delta\Phi_{J(\omega_0)} = \max_\theta \{ \Delta\Phi_{J(\omega_0)}^\theta \} - \min_\theta \{ \Delta\Phi_{J(\omega_0)}^\theta \} \quad \text{for } J = S, 0, +, -. \quad (3.60)$$

3.2 Reference-probe model

The so-called reference-probe model was established in previous works [102, 105, 106] as a conceptual model for understanding the directional effect of an external magnetic field. The assumption is that if the field influences the evolution of the electron spins of the two radicals in distinct ways, it will have a big impact on the spin dynamics of the radical pair. Thus, when the spin evolution on one radical is mostly unaffected by the external magnetic field and the spin evolution on the other radical is primarily controlled by the external magnetic field, an ideal directional sensitivity is expected to emerge. This suggests that an optimal radical pair would have no internal interactions in one radical (the *probe* radical),

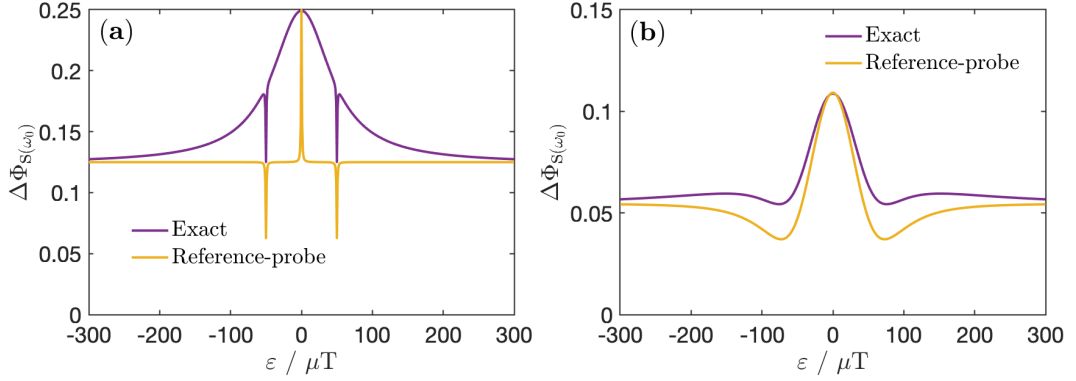


Figure 3.11: One-proton radical pair with $A_{zz} = 1.7$ mT and $\omega_0 = 50$ μ T. The exact and the reference-probe (i.e. artificially screening radical 1 from the external magnetic field) simulations for $\Delta\Phi_{S(\omega_0)} = \Phi_{S(\omega_0)}^z - \Phi_{S(\omega_0)}^x$ as a function of ε . $k = 10^5$ s $^{-1}$ for (a) and $k = 10^7$ s $^{-1}$ for (b).

with its electron spin evolution dictated solely by the Zeeman interaction, and strong hyperfine interactions in the other radical (the *reference* radical) dwarfing the effects of the weak external magnetic field.

We consider that the classical explanation for the reference radical in Ref [106] (i.e. regarding the hyperfine interactions as an internal magnetic field $\mathbf{A}_{\text{hf}}$ (a vector) which is far stronger than the external weak magnetic field so as to ignore its perturbation to $\mathbf{A}_{\text{hf}}$) is not appropriate. Based on the degenerate perturbation analysis, the weak magnetic field effect on the (nearly) degenerate subspaces of the spin Hamiltonian (not only the splitting of the energy levels but also the change in the eigenbasis) is absolutely quantum mechanical, and the classicalization of the hyperfine interactions destroys such subspaces induced by small hyperfine tensor components (e.g. A_{xx} and A_{yy} of the axial hyperfine tensor), through treating the component operators in the representation of hyperfine interactions as small vector components (e.g. taking $A_{xx}\hat{I}_x$ as $A_{xx}\langle\hat{I}_x\rangle$). Calculation for the realistic FAD-based radical pair in comparison with the semi-classical method [107] suggests the necessity of quantum mechanical treatment for the short-lived

radical pair to sense the direction of the weak magnetic field.

The change in the eigenbasis in the nearly degenerate subspaces can be characterized by the population contribution when calculating the singlet yield. The less the magnetic field can disturb the eigenbasis in the nearly degenerate subspace, the less the population contribution is, meaning that such radical has a good reference character. For the one-proton radical pair, the radical with the proton can be seen as not affected by the magnetic field when $|\varepsilon| \gg \omega_0$ (Figure 3.2). Therefore, artificially switching off the external magnetic field in this radical will not bring significant deviation from the exact simulation where both radicals experience the field (see Figure 3.11(a) and (b) when $|\varepsilon| > 200 \mu\text{T}$). Note that in Figure 3.11(a) when $|\varepsilon| \simeq 0 \ll k$, although the population contribution arrives at its maximum (see equation (3.33)), the reference-probe model matches satisfactorily with the exact simulation. This is because ε is too small to induce any appreciable conversion from $S(T_0)$ to $T_{\pm}$ during the radical pair lifetime, whereby it is appropriate to ignore such negligible hyperfine tensor components. Thus, the nearly degenerate subspace $\mathcal{H}^{34}$ can be approximately considered degenerate (so that the eigenbasis of $\mathcal{H}^{34}$ in equation (3.5) is equivalent to that in equation (3.24)). In this way, the concept of a population contribution becomes meaningless given that it is impossible to find a unique eigenbasis in the degenerate $\mathcal{H}^{34}$. Increasing the reaction rate constant to 10^7 s^{-1} in Figure 3.11(b) (equivalent to $\sim 50 \mu\text{T}$ in the Lorentzian function $f_{(\omega)}$), it is clear to see that the range of ε for a good matching of the reference-probe model with the exact simulation (i.e. $|\varepsilon| \ll k$) expands roughly from $|\varepsilon| \simeq 0$ to $|\varepsilon| \lesssim 20 \mu\text{T}$.

The eigenstructure of the potential reference radical resists the disturbance of the external magnetic field anisotropically with respect to the field direction

(see the degenerate perturbation analysis for the effect of a magnetic field along the z (or x) axis). A good reference character means that the nearly degenerate subspaces of this radical are difficult for the external magnetic field to reconstruct no matter where the field is oriented. This requires, from the analysis of the one-proton radical pair, that either (1) the energy gaps induced by the hyperfine interactions (including the small components, e.g. ε) are larger than the Zeeman splitting caused by the weak field; or (2) the spin interconversion in the nearly degenerate subspaces is far slower than the reaction rate constant, so that these subspaces are appropriately regarded as degenerate.

3.2.1 Correspondence between directional sensitivity and reference character

The directional sensitivity is normally quantified by $\Delta\Phi_{S(\omega_0)}$,

$$\Delta\Phi_{S(\omega_0)} = \max_{\theta}(\Phi_{S(\omega_0, \theta)}) - \min_{\theta}(\Phi_{S(\omega_0, \theta)}), \quad (3.61)$$

which is the difference between the maximum and minimum values of the singlet yield as a function of the field direction (which is characterized by the polar angle θ here). Ref. [106] provides a quantitative technique of measuring the reference character by defining an index “ R ” as:

$$R = \frac{\Delta\Phi_{S(\omega_0)}}{\xi} \quad (3.62)$$

where $\xi = \sqrt{\frac{\sum_{i=1}^N (\Phi_{S(\theta_i)} - \Phi_{S(\theta_i)}^{\text{ref}})^2}{N}}$ is the root-mean-square deviation in which i denotes the i -th angle, N is the number of computed angles and $\Phi_{S(\theta_i)}^{\text{ref}}$ denotes the singlet yield calculated with radical 1 artificially isolated from the external magnetic field for the reference-probe model. The larger R is, the better the reference-probe model matches the exact simulation, and the more differently the external magnetic field influences the spin evolution of the two radicals.

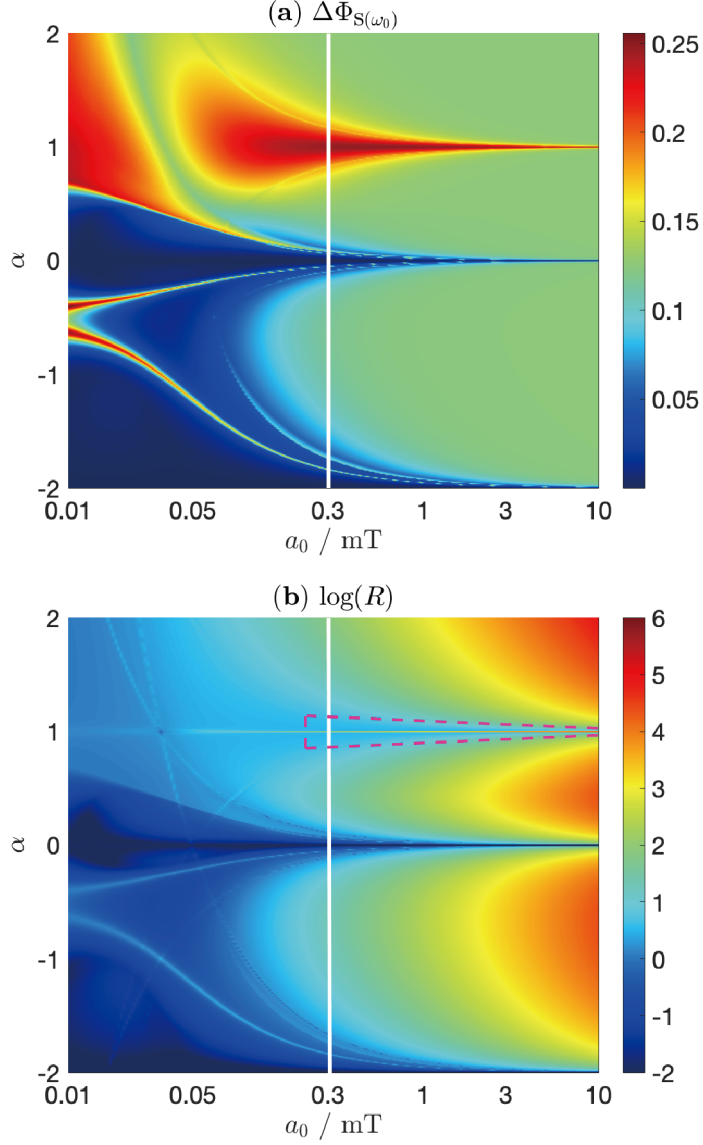


Figure 3.12: One-proton radical pair with an axial hyperfine interaction, $A_{xx} = A_{yy} = a_0(1 - \alpha)$, $A_{zz} = a_0(1 + 2\alpha)$, $\omega_0 = 50 \mu\text{T}$ and $k = 10^5 \text{ s}^{-1}$. (a) $\Delta\Phi_{\text{S}(\omega_0)}$ and (b) R as a function of a_0 and α ($0.01 < a_0 < 10 \text{ mT}$ and $-2 < \alpha < 2$). θ ranges from 0° to 90° with a step of 0.2° . The white line is plotted with $a_0 = 0.3 \text{ mT}$. The pink dashed area in (b) illustrates the region where α is in the vicinity of 1.

Figures 3.12(a) and (b) respectively show $\Delta\Phi_{\text{S}(\omega_0)}$ and $\log(R)$ as a function of the hyperfine parameters a_0 and α which characterize the axial hyperfine tensor of the proton (i.e. $A_{xx} = A_{yy} = a_0(1 - \alpha)$, $A_{zz} = a_0(1 + 2\alpha)$). The radical pair lifetime here is relatively long, $10 \mu\text{s}$, corresponding to a reaction rate constant $k = 10^5 \text{ s}^{-1}$. As is found in Ref [106], clear correspondence between $\Delta\Phi_{\text{S}(\omega_0)}$ and

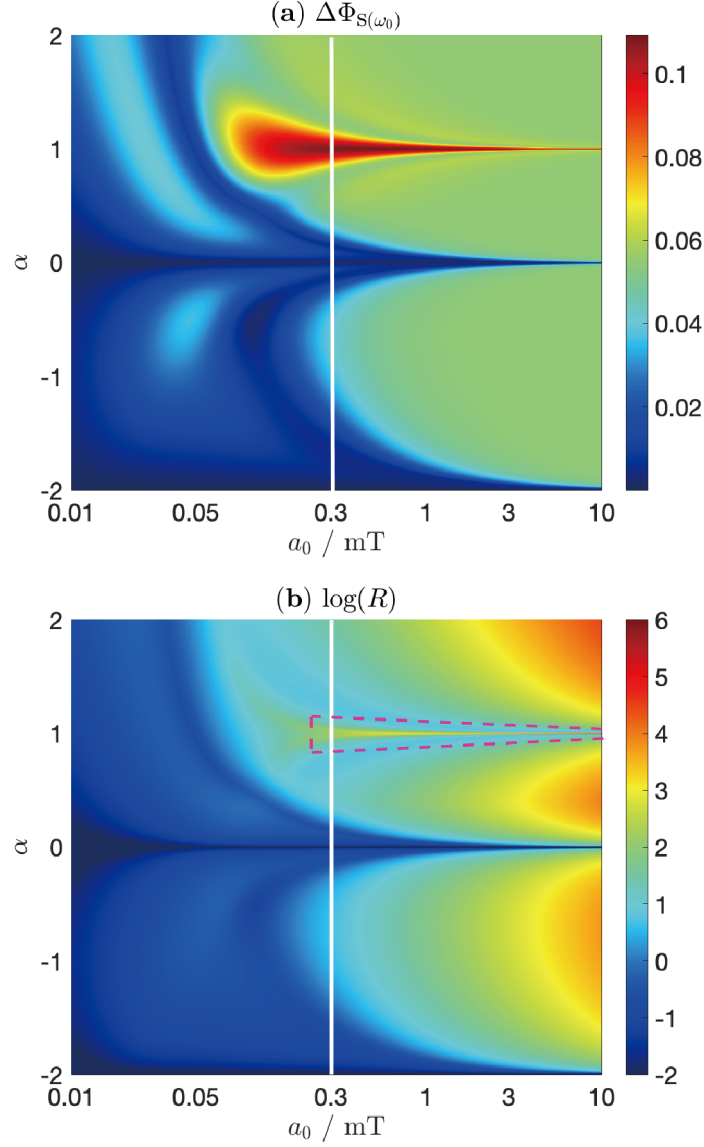


Figure 3.13: Same as Figure 3.10 but $k = 10^7 \text{ s}^{-1}$.

R can be seen, especially with $a_0 > 0.3 \text{ mT}$ (a region separated by the white solid line) such that the external magnetic field ($\omega_0 = 50 \mu\text{T}$) is considered far weaker than the hyperfine interaction. As α becomes close to 0 ($A_{xx} = A_{yy} = A_{zz} = a_0$) or -2 ($A_{xx} = A_{yy} = -A_{zz} = 3a_0$), the directional sensitivity drops, and the reference character declines simultaneously. Note that when α is in the vicinity of 1, demonstrated by the pink dashed area in Figure 3.12(b), (equivalent to $k \lesssim |\varepsilon| \lesssim \omega_0$), the $R - \Delta\Phi_{S(\omega_0)}$ correspondence breaks: high directional sensitivity

but low reference character, as a result of the non-negligible change in the eigenbasis in the nearly degenerate subspaces as already discussed (see Figure 3.11). In Figure 3.13(a) and (b), k is raised to 10^7 s^{-1} . The correspondence can still be clearly seen, and in the pink dashed region, the requirement for α to obtain a high R (Note that $\log(R) \gtrsim 1$ is regarded as a high R , which will be discussed later) becomes less strict in contrast to the case of $k = 10^5 \text{ s}^{-1}$ where α must be 1. Thus, it is natural to speculate that such good correspondence between $\Delta\Phi_{S(\omega_0)}$ and R , which is not easily influenced by the reaction rate constants, could possibly be a basis for the study of a potential chemical magnetoreceptor without carrying out the complex calculation of the spin selective reaction process, instead, through the insights into the insensitivity of the reference radical to the weak magnetic field. Furthermore, if the reference-probe model works, spin dynamics simulations will be greatly accelerated [102] if the reference radical has a large number of nuclear spins. The time-consuming calculation for the reference radical only has to be done once by switching off its interaction with the external magnetic field of various directions.

3.2.2 Disruption by the inter-electron spin interaction

So far, the inter-radical interactions have been ignored throughout the calculation. We suspect that the correspondence between the directional sensitivity and the reference character can be fatally disrupted if interactions, such as the dipolar interaction, are included, given that they link the separated spin spaces (characterized by Zeeman and hyperfine interactions) of the two radicals. Then, artificially switching off the magnetic field for one radical risks deviating from the actual spin dynamics of the radical pair, even if the hyperfine interaction eigenspace of the reference radical is not disturbed directly by the Zeeman interaction with the weak external field.

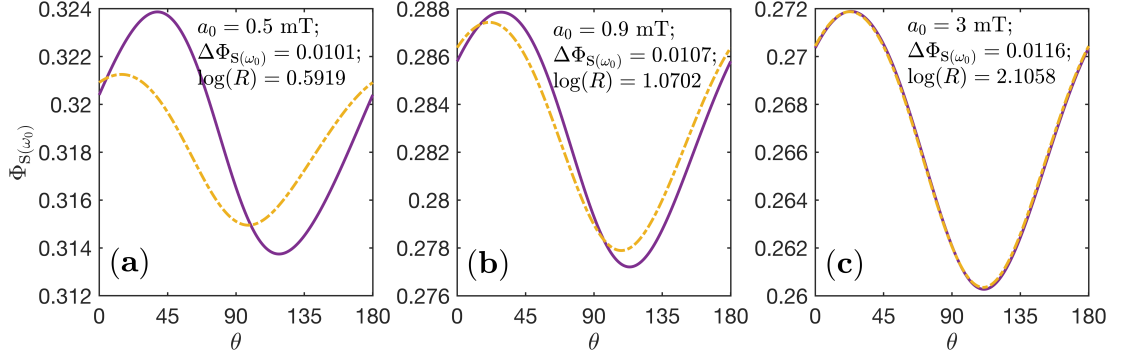


Figure 3.14: Singlet yield as a function of the magnetic field direction, characterized by the polar angle θ in degrees, for $\alpha = 1$ and $a_0 = 0.5, 0.9$ and 3 mT. The purple solid lines show the exact simulation, and the orange dash-dotted lines show the reference-probe model results. $\omega_0 = 50 \mu\text{T}$, $k = 10^5 \text{ s}^{-1}$. The $-510.6 \mu\text{T}$, $\theta_D = 60^\circ$ dipolar interaction is included.

The singlet yield of the one-proton radical pair with a dipolar interaction is calculated as a function of the field direction (Figure 3.14). Note that the dipolar interaction is $-510.6 \mu\text{T}$ corresponding to 1.76 nm radical-radical separation and the vector joining the radicals is 60° relative to the z -axis. The polar angle (θ) of the field direction varies from 0° to 180° , and the azimuthal angle ϕ of the field direction is 0 . We compare the exact simulation with the reference-probe model for three values of the hyperfine parameter: $a_0 = 0.5 \text{ mT}$ for Figure 3.14(a); $a_0 = 0.9 \text{ mT}$ for Figure 3.14(b); $a_0 = 3 \text{ mT}$ for Figure 3.14(c). Let $\alpha = 1$, so that the hyperfine eigenbasis of the reference radical is not influenced by the external magnetic field. Including the dipolar interaction, we find: the reference-probe model completely fails (Figure 3.14(a)) at $a_0 = 0.5 \text{ mT}$ where $\log(R) = 0.59$; the reference-probe model adequately matches the exact simulation (Figure 3.14(b)) at $a_0 = 0.9 \text{ mT}$ where $\log(R) = 1.07$, so that $\log(R) \gtrsim 1$ is taken as the threshold value for a working reference-probe model; the reference-probe model satisfactorily agrees with the exact simulation (Figure 3.14(c)) at $a_0 = 3 \text{ mT}$ where $\log(R) = 2.11$. Although the directional sensitivity ($\Delta\Phi_{s(\omega_0)}$) and the anisotropy pattern of the singlet yield (i.e. the shape of the purple solid traces) are similar for the three values of a_0 , the reference characters ($\log(R)$) show great difference,

3.2. Reference-probe model

indicating that the correspondence between $\Delta\Phi_{s(\omega_0)}$ and R vanishes.

The reference-probe model is possibly valuable on condition that the hyperfine interaction is stronger than the dipolar interaction (remembering $a_0 = 0.9$ mT gives $\log(R) = 1.07$). The axial hyperfine interactions of the electron with the two nitrogens in FAD (Appendix A), considered as the main source of the directional sensitivity of the avian magnetic compass [63, 102], are both smaller than $600 \mu\text{T}$, not appreciably greater than the reasonable dipolar interaction ~ 350 to $567 \mu\text{T}$ (corresponding to a radical separation from 1.7 to 2.0 nm [79]). Nevertheless, it is too early to assert that the reference-probe model entirely fails on the FAD-based radical pair with a centre-centre separation 1.7-2.0 nm, given that the one-proton radical pair oversimplifies the spin dynamics of a realistic radical pair with multiple hyperfine interactions.

3.2.3 FAD-based radical pair

As discussed in Chapter 1, the cryptochrome (Cry) protein, found in the retinas of several bird species, remains the most likely candidate for the chemical magnetic compass for avian navigation [79, 108] since first proposed in 2000 [52]. The radical pairs are formed by sequential electron transfers after photo-excitation (light wavelength approximately in the range 300 – 500 nm) of the FAD cofactor that binds to the protein [79]. A computational study on the comparison of the reference-probe model with the exact simulation for several potential radical pairs in Cry will be shown below to evaluate the reference-probe model for FAD-based radical pairs.

FAD-Z radical pair

Behavioural experiments [48] on European robins under extraordinarily weak (~ 15 nT) oscillating magnetic fields showed that the magnetic orientation of

birds seemed to be disrupted by time-dependent fields oscillating at the Larmor frequency for a free electron in Earth’s magnetic field (~ 1.3 MHz corresponding to the local geomagnetic field of $46 \mu\text{T}$). Although such remarkable observation has not been replicated by later experiments [49], the resonant response to the oscillating field at the Larmor frequency requires that one of the radicals has to be isolated from the intra-radical hyperfine interactions (i.e. the radical is devoid of nuclear spins) [109]. We refer to this radical as $Z^\bullet$, which can be positively or negatively charged or neutral.

The identity and existence of $Z^\bullet$ is still of mystery - several possible candidates are introduced in Ref [102], among which superoxide $\text{O}_2^{\bullet-}$ is considered. In the reaction scheme of radical pairs in Cry [102, 110], superoxide is possibly produced through the reoxidation of the fully reduced FAD by oxygen: $\text{FADH}^- + \text{O}_2 \rightarrow [\text{FADH}^\bullet \text{O}_2^{\bullet-}]$ [111–113], where FADH^- can be obtained through photo-induced electron transfer under light of wavelength less than 650 nm from the protonated $\text{FAD}^{\bullet-}$, i.e. the long-lived $\text{FADH}^\bullet$. The restrictive conditions, for a valid flavin-superoxide based compass sensor, on the local environment (characterized by a ligand field with contribution to the quenching of the electron’s orbital angular momentum in $\text{O}_2^{\bullet-}$) and the molecular dynamics (so as to the spin relaxation induced by the spin-orbit coupling in $\text{O}_2^{\bullet-}$) are given in Ref [110]. Furthermore, as is mentioned in Ref [102], a $Z^\bullet$ radical could be directly formed, either by an electron donor bound to Cry with competitively fast electron transfer, in comparison with that from the Trp-triad, to the photo-excited FAD: $\text{FAD}^* + \text{D} \rightarrow [\text{FAD}^{\bullet-} \text{D}^{\bullet+}]$, or by an external electron donor *in vivo* to reduce the $\text{TrpH}^{\bullet+}$ radical in $[\text{FAD}^{\bullet-} \text{TrpH}^{\bullet+}]$: $[\text{FAD}^{\bullet-} \text{TrpH}^{\bullet+}] + \text{D} \rightarrow [\text{FAD}^{\bullet-} \text{D}^{\bullet+}] + \text{TrpH}$.

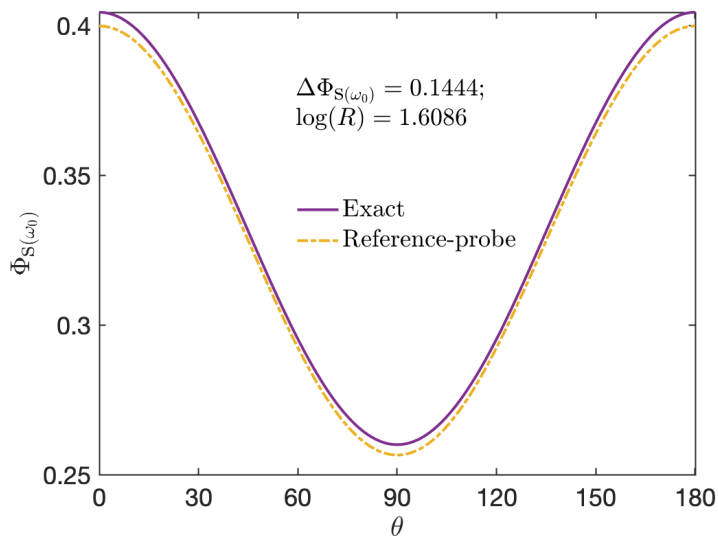


Figure 3.15: Singlet yield as a function of the magnetic field direction, characterized by the polar angle θ for a realistic FAD-Z radical pair including the seven largest hyperfine interactions in the $\text{FAD}^{\bullet-}$ radical. The purple solid lines show the exact simulation, and the orange dash-dotted lines show the reference-probe model results. $\omega_0 = 50 \mu\text{T}$, $k = 10^6 \text{ s}^{-1}$. No inter-radical interaction has been included.

The directional sensitivity of the FAD-Z radical pair, evaluated in detail in Ref [102], is superior (with > 100 times greater $\Delta\Phi_{S(\omega_0)}$) than that of a FAD-Trp radical pair. It is clear to see in Figure 3.15 that the reference-probe model works satisfactorily (with $\log(R) = 1.6$) for the FAD-Z radical pair without the inter-radical interactions, meaning that the electron spin motion of the $\text{FAD}^{\bullet-}$ radical as the reference radical is dominated by the internal hyperfine interactions, and the weak magnetic field is unable to notably affect the spin dynamics of the $\text{FAD}^{\bullet-}$ radical [102, 106]. Such good reference character of the $\text{FAD}^{\bullet-}$ radical, indicating the FAD-Z radical pair could be an optimal magnetic sensor, is under the approximation condition that the two radicals are so far apart ($r \gtrsim 3.5 \text{ nm}$) that the inter-radical interactions, e.g. the dipolar interaction, can be appropriately ignored. However, this assumption leads to a lifetime that is too long for the weak magnetic field to modulate the yields of the reaction products, as the coherent spin states would be completely relaxed before the recombination of a significant

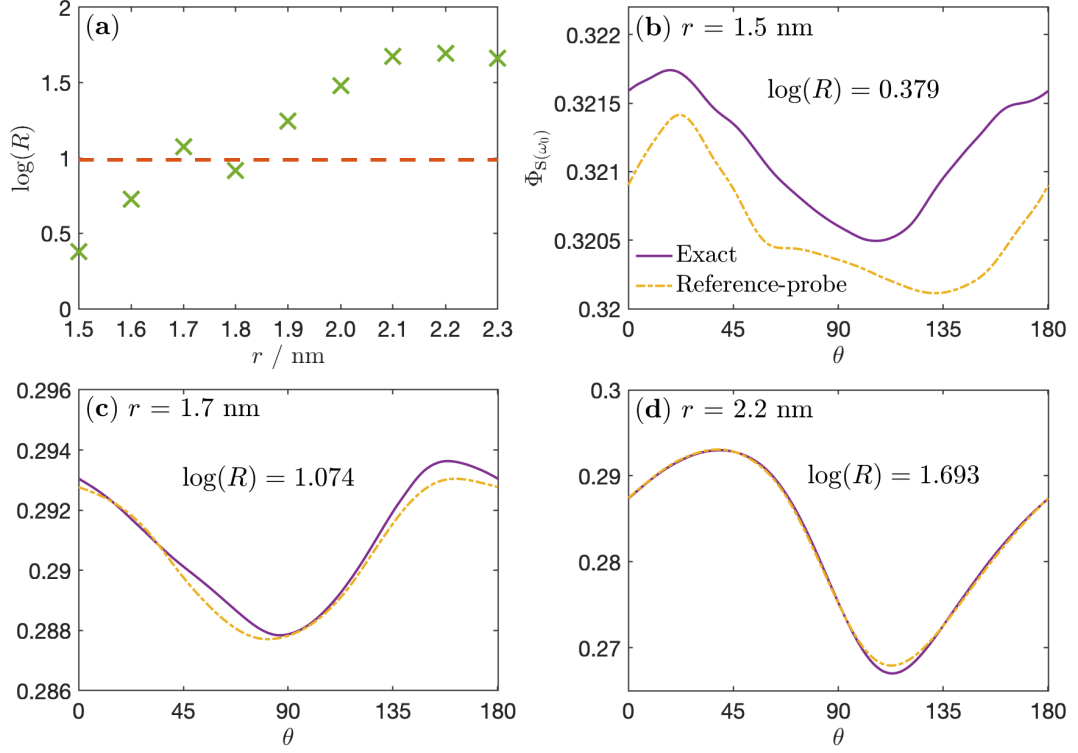


Figure 3.16: Singlet yield as a function of the magnetic field direction, characterized by the polar angle θ in degrees, for a realistic FAD-Z radical pair including the seven largest hyperfine interactions in the $\text{FAD}^{\bullet-}$ radical. The purple solid lines show the exact simulation, and the orange dash-dotted lines show the reference-probe model results. $\omega_0 = 50 \mu\text{T}$, $k = 10^6 \text{ s}^{-1}$. No inter-radical interaction has been included.

fraction of the radical pairs [63]. In Section 3.2.2, we saw that a dipolar interaction, comparable to the hyperfine interaction, can destroy the reference character for the one-proton radical pair. Varying centre-centre separation of FAD-Z radical pairs allows us to see how the reference character of the more realistic $\text{FAD}^{\bullet-}$ radical, including the seven largest hyperfine interactions (Appendix A), could resist the dipolar interaction. In Figure 3.16, the reference-probe model agrees with the exact simulation to an acceptable extent (i.e. $\log(R) \gtrsim 1$) for $r > 1.7$ nm. Beyond this centre-centre separation, the external magnetic field would affect the spin evolution of the two radicals in an optimal different fashion, which correspondently gives rise to a good directional sensitivity.

FAD-X radical pair

The existence of the FAD-Z radical pair is still speculative, as birds' disorientation under an RF field at the Larmor frequency was not seen by Schwarze *et al* in 2016 [49]. It is a restrictive condition for most organic radicals to have no hyperfine interactions, as an organic radical typically has at least one ^1H or ^{14}N atom in the neighbourhood of the semi-occupied molecular orbital. Thus, the question, whether the reference-probe model remains valid when there are non-negligible hyperfine interactions in the probe radical (such that the spin dynamics of the electron in this radical is not only controlled by the external magnetic field), becomes significant for a general use of this proposed model.

We start with a toy radical containing one proton as the probe radical, in which the hyperfine interaction is isotropic (the hyperfine parameter is $500\text{ }\mu\text{T}$). We only include the two axial nitrogens, which accounts for the directional sensitivity

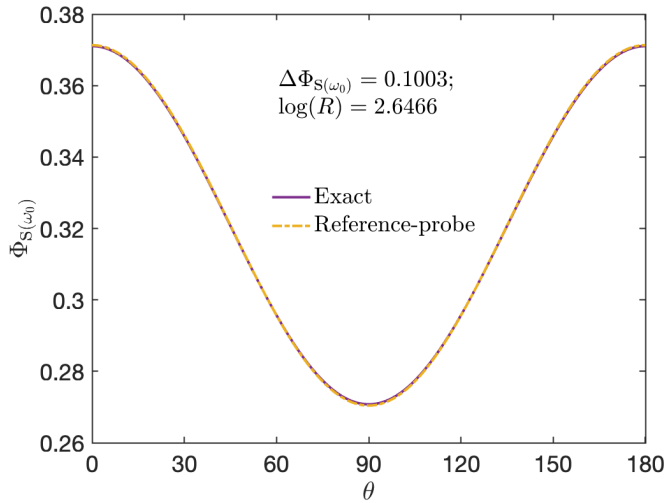


Figure 3.17: Singlet yield as a function of the magnetic field direction, characterized by the polar angle θ in degrees, for a FAD-X radical pair. The two axial nitrogens are included in the $\text{FAD}^{\bullet-}$ radical, and a ^1H nucleus with an isotropic hyperfine interaction of $500\text{ }\mu\text{T}$ is included in the other radical. $\omega_0 = 50\text{ }\mu\text{T}$, $k = 10^6\text{ s}^{-1}$. No inter-radical interaction has been included.

[102], in $\text{FAD}^{\bullet-}$ as the reference radical. As our main goal here is to investigate the effect of the hyperfine interactions in the probe radical on the validity of the reference-probe model, we temporarily ignore the dipolar interaction. It is clear to see in Figure 3.17 that the reference-probe model perfectly matches the exact simulation, even though the spin evolution of the probe radical is not solely driven by the external magnetic field. Based on this simple case, we suspect that the probe radical can still accurately detect the direction of the magnetic field if the internal fields characterized by the hyperfine interactions are **isotropic**. In order

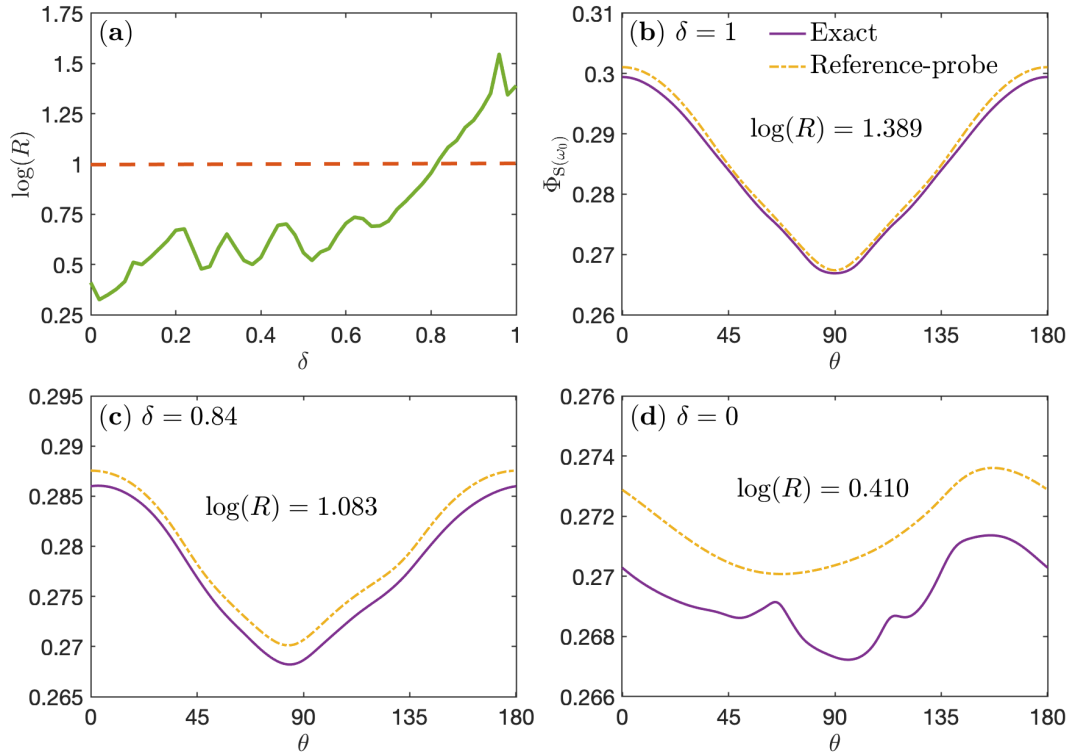


Figure 3.18: A radical pair in which radical 1 has the two axial nitrogens of $\text{FAD}^{\bullet-}$ and radical 2 is an artificial radical where there are four ^1H nuclei, all of which have axial hyperfine interactions. The symmetry axes of the four hyperfine tensors are directed towards the vertices of a tetrahedron. $\omega_0 = 50 \mu\text{T}$, $k = 10^6 \text{ s}^{-1}$. No inter-radical interaction has been included. (a) depicts R , in logarithmic scale, as a function of δ . For the calculation of R , the field direction is characterized by the polar angle θ ranging from 0 to π with a step of $\pi/40$ and the azimuthal angle ϕ ranging from 0 to 2π with a step of $\pi/20$. (b), (c) and (d) show the singlet yield as a function of θ in degrees with $\phi = 0$ for three values of δ .

3.2. Reference-probe model

to demonstrate the relation between the internal fields and the reference-probe model, we exploit an artificial radical that was previously introduced in Ref. [114]. In one radical, N5 and N10 of $\text{FAD}^{\bullet-}$ are included, and in the other radical as the proposed artificial radical, four ^1H with tetrahedrally disposed axial hyperfine tensors are included. Three of these tensors have principal values: $A_{11} = A_{22} = -1$, $A_{33} = 2$ mT. The fourth is identical apart from a uniform scaling of the principal values by a factor δ ranging from 0 to 1. $\delta = 1$ (i.e. the principal values of all the four hyperfine tensors are equal) indicates that the internal fields of such artificial radical can be considered isotropic [114], whereas $\delta < 1$ gives rise to an anisotropic internal field environment. In Figure 3.18 (a), the reference-probe model can be trusted only when δ is assigned with a high value (i.e. $\delta \gtrsim 0.84$ leads to $\log(R) \gtrsim 1$). In Figure 3.18 (b), (c) and (d), we can see that the threshold value, $\log(R) \gtrsim 1$, to indicate a valuable reference-probe model still works. Now we can draw a safe conclusion that the validity of the reference-probe model relies on the isotropy of the internal field environment of the probe radical. A common biological reductant called ascorbic acid can create a radical, where there are a few isotropic hyperfine interactions [102], by reducing photoexcited flavin

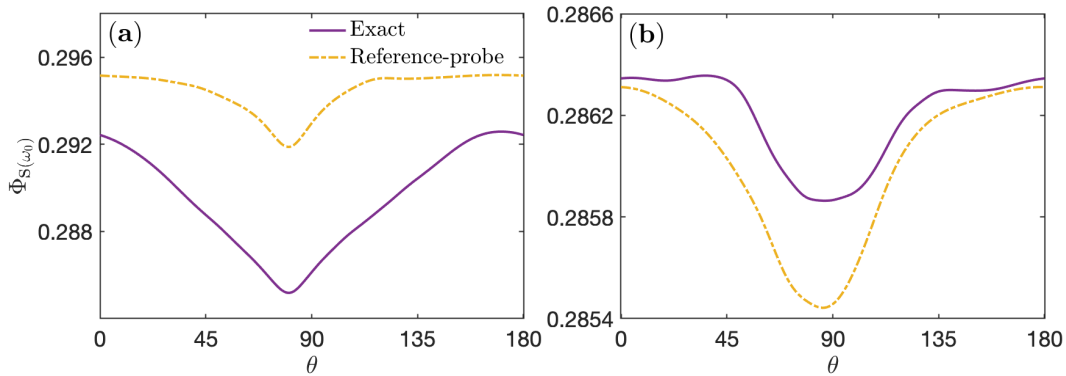


Figure 3.19: Singlet yield as a function of θ with $\phi = 0$ for the FAD-TrpH radical pair. The two nitrogens, N5 and N10, are included in $\text{FAD}^{\bullet-}$, and six nuclei, N1, H1, H2, H4, H7 and H β , are included in $\text{TrpH}^{\bullet+}$. $\omega_0 = 50$ μT , $k = 10^6$ s^{-1} . No inter-radical interaction is included in (a); a dipolar interaction of -0.4 mT, corresponding to the ~ 1.9 nm separation of $\text{FAD}^{\bullet-}$ and $\text{TrpH}^{\bullet+}$, is included in (b).

[115] and Trp radicals [116]. We compare the reference-probe model with the exact simulation on this potential radical pair, and find they match satisfactorily well with a directional sensitivity $\Delta\Phi_S = 0.098$ and a good reference character $\log(R) = 2.47$. As for the FAD-Trp radical pair, the most likely candidate that is responsible for avian magnetoreception, the reference-probe model unfortunately fails no matter whether the dipolar interaction is taken into account (Figure 3.19). This means that the $\text{TrpH}^{\bullet+}$ radical cannot provide a satisfactory isotropic internal field environment for the unpaired electron to make an eligible probe radical, though six nuclei of $\text{TrpH}^{\bullet+}$ with the largest anisotropic hyperfine interactions (Appendix A) have been included in the calculation.

3.2.4 Conclusion

The reference-probe model originates in the assumption that a radical pair, where the spin evolution of one radical is not disturbed by the external magnetic field but entirely driven by the internal hyperfine interactions and the spin evolution of the other radical is solely dependent on the external field, gives an optimal condition that the field tends to affect the two radicals in the most different fashion thereby modulating the spin interconversion in the radical pair to the largest extent [102, 106]. Therefore, the directional sensitivity is supposed to arrive at its maximum, since the magnetic field direction is directly accurately reflected by the spin dynamics of the probe radical. Computational investigation for the one-proton radical pair gives a clear correspondence between the directional sensitivity and the reference character, an index that quantifies how the reference-probe model matches the exact simulation, provided that either the eigenstructure of the reference radical is immune from the external magnetic field, or the energy gaps (in units of angular frequency) in the nearly degenerate subspaces of the hyperfine interactions are negligible relative to the reaction rate constant (e.g.

$|\varepsilon| \ll k$). Such correspondence makes it promising to only look at the candidate reference radical so as to evaluate a potential radical-pair based magnetic compass. However, the inclusion of the non-negligible inter-radical interactions such as the dipolar interaction can destroy such correspondence, which questions the validity of the reference-probe model even if the reference radical could perfectly resist the perturbation of the external field.

Investigation of the FAD-based radical pair clearly shows that the flavin radical, when paired with a radical with no magnetic nuclei (a probe radical), reveals a great reference character thereby giving a good directional sensitivity. Even though a dipolar interaction is considered, the $\text{FAD}^{\bullet-}$ radical maintains such outstanding reference character with reasonable centre-centre separation ($\gtrsim 1.7$ nm). Furthermore, we find that a working reference-probe model does not require the radical paired with $\text{FAD}^{\bullet-}$ to be isolated from magnetic nuclei. As long as the internal fields arising from the hyperfine interactions are highly isotropic, the reference-probe model can still work satisfactorily. We can envisage radicals such as the ascorbyl radical which tumble rapidly to average out the anisotropic parts of the hyperfine interactions to provide such an isotropic internal field environment. Unfortunately, the $\text{TrpH}^{\bullet+}$ radical, which is considered the most probable radical paired with $\text{FAD}^{\bullet-}$ in Cry, does not meet this condition for the reference-probe to work.

Chapter 4

Orientation of birds in radiofrequency fields – a possible test for the radical pair mechanism of magnetoreception

Firstly proposed by Ritz *et al.* in 2004 [46], the effect of radiofrequency (RF) electromagnetic fields on the orientational behaviour of migratory birds offers a strong supporting evidence of the magnetic compass based on the radical pair mechanism rather than the magnetite hypothesis. RF fields, in resonance with the singlet-triplet interconversion frequencies arising from the electron spin interactions with the static field or the intra-radical nuclear spins, alter the reaction yield [40–45] that encodes the directional magnetic-field dependence. The application of RF fields can remove the anisotropy of reaction yield, which accounts for the disruption of birds' ability to orient in Earth's magnetic field in the frame of radical pair mechanism. The disorientation of birds continued to be reported by behavioural experimental studies [47–49, 117, 118], using single-frequency or broadband electromagnetic fields, following the original one in Ref. [46]. Significantly, a distinct resonance at the Larmor frequency - the precession frequency of a free electron spin in Earth's magnetic field is reported [48], which is interpreted to mean that one of the radicals has an electron solely interacting with the external

fields (i.e. the “Z radical” in Chapter 3).

However, both the monochromatic and noise-modulated RF fields used in these studies, at the orders of 10-100 nT, are far too weak to have a large effect on a biologically plausible radical pair with a lifetime of $\sim 1 \mu\text{s}$. A monochromatic RF field of 25 nT needs at least 200 μs to have a noticeable effect on the radical-pair spin dynamics [119]. The requirement of such long time is far beyond the most generous estimates of the spin relaxation times of organic radicals in the warm and noisy environment of a living cell. This has led to speculation that the observed disorientation might result from some unknown effect of the electric component of the electromagnetic field or an unknown effect on the magnetic signalling mechanism or on the birds’ motivation [109].

Laboratory studies of organic radical pairs have demonstrated that RF fields applied in the absence of a static field can still alter reaction yields [40, 45]. This suggests that it might be possible to orient birds in the absence of the geomagnetic field by subjecting them to a resonant RF field of comparable strength to the Earth’s field. This would constitute a more convincing test - reorientation rather than disorientation in an RF field under very carefully controlled conditions on its strength and frequency, for the operation of a radical-pair based compass. It is difficult to imagine that an RF effect on anything other than the primary magnetic detection events would lead to orientation in the direction of the time-dependent field. It is also unclear how a magnetite-based compass sensor would be sensitive to a magnetic field that reverses several million times per second. Any magnetite crystal large enough to have a $> k_{\text{B}}T$ interaction with the geomagnetic field would be too large to reorient in a ca. 1 MHz field. Therefore, we have theoretical insights into the effect of a RF field on the spin evolution of a radical pair and

use spin dynamics simulations to explore the possibility that a radical pair could provide a bird with the information it needed to be able to orient in an RF field in the absence of the geomagnetic field.

4.1 Non-degenerate resonance

Unlike a weak static magnetic field which boosts the singlet-triplet interconversion mainly by lifting the degeneracy of energy levels [54], an RF field can potentially affect the interconversion via inducing resonance between eigenstates of the spin Hamiltonian for the radical pair. The application of an RF field makes the Hamiltonian dependent on time such that it is difficult to obtain an exact solution for the time evolution of the system. Instead of starting with a large realistic spin system, it is useful to firstly look into the evolution of a simple two-level system.

4.1.1 Two-level system

Consider a simple two-level system with a Hamiltonian that has the matrix form,

$$\hat{H}_0 = \begin{pmatrix} \omega_1 & 0 \\ 0 & \omega_2 \end{pmatrix}, \quad (4.1)$$

where ω_1 and ω_2 are the energy eigenvalues for the two eigenstates,

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (4.2)$$

respectively. Let the singlet and triplet states (i.e. $|S\rangle$ and $|T\rangle$) be two orthogonal non-stationary states in the eigenbasis,

$$|S\rangle = a|1\rangle + b|2\rangle, \quad |T\rangle = -b|1\rangle + a|2\rangle, \quad (4.3)$$

where $a^2 + b^2 = 1$ (note that a and b are real for simplicity). Their interconversion is driven by $\hat{H}_0$ and the time-dependent probability of the triplet state is

$$P_{(t)}^T = |\langle T | e^{-i\hat{H}_0 t} | S \rangle|^2 = 2(1 - \cos(\omega_{21} t))a^2b^2, \quad (4.4)$$

4.1. Non-degenerate resonance

where we assume that the initial state is $|S\rangle$ and $\omega_{21} = \omega_2 - \omega_1 > 0$. The applied oscillating RF field is represented as

$$\hat{H}'_{(t)} = \begin{pmatrix} 0 & V e^{i\omega t} \\ V e^{-i\omega t} & 0 \end{pmatrix}, \quad (4.5)$$

where ω is the oscillation frequency. The total Hamiltonian is $\hat{H}_{(t)} = \hat{H}_0 + \hat{H}'_{(t)}$ and the exact solution for the time-evolution propagator is difficult to find. Instead, taking $\hat{H}'_{(t)}$ as a time-dependent perturbation to $\hat{H}_0$ (i.e. $V \ll |\omega_1 - \omega_2|$) would give an approximate solution. In the interaction picture (Appendix C), the dynamical equation for the state is

$$i \frac{d}{dt} |\tilde{\psi}_{(t)}\rangle = \hat{H}'_{(t)} |\tilde{\psi}_{(t)}\rangle, \quad (4.6)$$

where “ $\sim$ ” indicates the interaction picture as in Chapter 2. Thus $|\tilde{\psi}_{(t)}\rangle$ can be written in the eigenbasis of $\hat{H}_0$,

$$|\tilde{\psi}_{(t)}\rangle = \sum_{n=1,2} c_{n(t)} e^{i\omega_n t} |n\rangle = \sum_{n=1,2} \tilde{c}_{n(t)} |n\rangle, \quad (4.7)$$

where $\tilde{c}_{n(t)} = c_{n(t)} e^{i\omega_n t}$. Expanding $\tilde{c}_{n(t)}$ in the power of the perturbation V gives

$$\tilde{c}_{n(t)} = \tilde{c}_{n(t)}^{(0)} + \tilde{c}_{n(t)}^{(1)} + \tilde{c}_{n(t)}^{(2)} + \mathcal{O}(V^3). \quad (4.8)$$

Confine the perturbation analysis to first order:

$$\tilde{c}_{n(t)} \approx \tilde{c}_{n(t)}^{(0)} + \tilde{c}_{n(t)}^{(1)}, \quad (4.9)$$

and according to the time-dependent perturbation theory in Appendix C, we have:

$$\begin{aligned} \tilde{c}_{n(t)}^{(0)} &= c_{n(0)}, \\ \tilde{c}_{n(t)}^{(1)} &= -i \sum_{m=1,2} \int_0^t e^{i\omega_{nm} t'} H'_{(t)nm} c_{m(0)} dt', \end{aligned} \quad (4.10)$$

where $H'_{(t)nm} = \langle n | \hat{H}'_{(t)} | m \rangle$. Note that $V^2 t^2 \ll 1$ gives a satisfactory first-order perturbative result, such condition is reasonably met for a radical pair with a

lifetime $\sim 1 \mu\text{s}$ under an RF field at the order of $10 \mu\text{T}$. Using equation (4.10),

$$\begin{aligned}\tilde{c}_{1(t)}^{(0)} &= a, \quad \tilde{c}_{2(t)}^{(0)} = b, \\ \tilde{c}_{1(t)}^{(1)} &= bV \frac{e^{-i\Delta\omega t} - 1}{\Delta\omega} = bV \frac{-i\Delta\omega t - \frac{1}{2}\Delta\omega^2 t^2 + \mathcal{O}(\Delta\omega^3 t^3)}{\Delta\omega}, \\ \tilde{c}_{2(t)}^{(1)} &= aV \frac{1 - e^{i\Delta\omega t}}{\Delta\omega} = aV \frac{-i\Delta\omega t + \frac{1}{2}\Delta\omega^2 t^2 + \mathcal{O}(\Delta\omega^3 t^3)}{\Delta\omega},\end{aligned}\tag{4.11}$$

where $\Delta\omega = \omega_{21} - \omega$. Notice that the resonance of the RF field with the energy gap requires $\Delta\omega \rightarrow 0$. Thus, $\tilde{c}_{1(t)}^{(1)} \approx -ibVt$ and $\tilde{c}_{2(t)}^{(1)} \approx -iaVt$. Then,

$$\tilde{c}_{1(t)} = a - ibVt, \quad \tilde{c}_{2(t)} = b - iaVt.\tag{4.12}$$

Transforming back to the Schrödinger picture gives

$$c_{1(t)} = \frac{a - ibVt}{\sqrt{1 + V^2 t^2}} e^{-i\omega_1 t}, \quad c_{2(t)} = \frac{b - iaVt}{\sqrt{1 + V^2 t^2}} e^{-i\omega_2 t},\tag{4.13}$$

where $c_{1(t)}$ and $c_{2(t)}$ are scaled by $1/\sqrt{1 + V^2 t^2}$ to maintain $|c_{1(t)}|^2 + |c_{2(t)}|^2 = 1$. Then, $|\psi(t)\rangle = c_{1(t)}|1\rangle + c_{2(t)}|2\rangle$ and $P_{(t)}^T$ under a resonant RF field is obtained as

$$\begin{aligned}P_{(t)}^T &= |\langle T | \psi(t) \rangle|^2 \\ &= 2(1 - \cos(\omega_{21} t))a^2 b^2 + \frac{(a^2 - b^2)^2 V^2 t^2 + 2Vt \sin(\omega_{21} t)(a^2 - b^2)ab}{1 + V^2 t^2}.\end{aligned}\tag{4.14}$$

Importantly, $a = 1$ (so $b = 0$), i.e. $|S\rangle = |1\rangle$ and $|T\rangle = |2\rangle$, gives the typical Rabi oscillation, where $c_{1(t)}$ and $c_{2(t)}$ have the exact solution [85]:

$$\begin{aligned}|c_{2(t)}|^2 &= \frac{V^2}{V^2 + \frac{(\omega_{21} - \omega)^2}{4}} \sin^2 \left(\sqrt{V^2 + \frac{(\omega_{21} - \omega)^2}{4}} t \right), \\ |c_{1(t)}|^2 &= 1 - |c_{2(t)}|^2.\end{aligned}\tag{4.15}$$

Satisfying the resonance condition, $\omega_{21} = \omega$, gives

$$|c_{2(t)}|^2 = \sin^2(Vt), \quad |c_{1(t)}|^2 = \cos^2(Vt),\tag{4.16}$$

so that

$$P_{(t)}^T = |\langle T | \psi(t) \rangle|^2 = |c_{2(t)}|^2 = \sin^2(Vt).\tag{4.17}$$

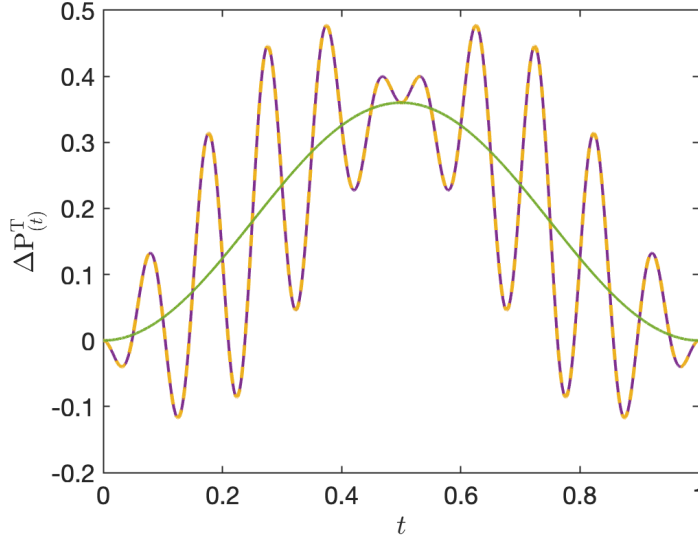


Figure 4.1: Resonance effect on the evolution of the simple two-level system. Change in the triplet probability, $\Delta P_{(t)}^T$, brought about by a resonant RF field is illustrated, by the purple solid trace using the exact numerical method in equation (4.19) and by the orange dashed trace using the analytical method in equation (4.18). The green solid trace denotes the transition term, $(a^2 - b^2)^2 \sin^2(Vt)$, in equation (4.18). The parameters in the calculation: $\omega_1 = 10 \times 2\pi$, $\omega_2 = 20 \times 2\pi$, $\omega = 10 \times 2\pi$ and $V = 0.5 \times 2\pi$.

Equation (4.14) should be able to reduce to equation (4.17) when $a = 1$ and $b = 0$. Hence, we speculate that $Vt/(1 + V^2t^2)$ from the perturbation theory is equivalent to $\sin(Vt)$ under short time limit (i.e. $V^2t^2 \ll 1$). Therefore, remembering equation (4.4) and (4.14), the exact solution for the change in $P_{(t)}^T$ brought about by the application of the resonant RF field could be:

$$\Delta P_{(t)}^T = (a^2 - b^2)^2 \sin^2(Vt) + \sin(2Vt) \sin(\omega_{21}t)(a^2 - b^2)ab. \quad (4.18)$$

Equation (4.18) is verified by the exact numerical simulation (Figure 4.1),

$$\Delta P_{(t)}^T = |\langle T | \hat{\mathcal{T}} e^{\int_0^t -i\hat{H}(\tau)d\tau} | S \rangle|^2 - |\langle T | e^{\hat{H}_0 t} | S \rangle|^2, \quad (4.19)$$

where $\hat{\mathcal{T}}$ is the Dyson time-ordering operator [85]. Equation (4.18) is thus the exact solution. Furthermore, under symmetric reaction approximation in Chapter 2 ($k = k_S = k_T$), the change in the yield of the triplet recombination brought

about by the resonant RF field is

$$\Phi_T = k \int_0^\infty \Delta P_{(t')}^T e^{-kt'} dt'. \quad (4.20)$$

The oscillatory term in equation (4.18), $\sin(2Vt) \sin(\omega_{21}t)(a^2 - b^2)ab$, describing the effect of the RF field on the dynamics of the coherence, ab , will be averaged out, as ω_{21} is assumed to exceed the reaction rate constant. Thus, it is the transition term, $(a^2 - b^2)^2 \sin^2(Vt)$ (i.e. the green trace in Figure 4.1), that is primarily responsible for the resonance effect on the radical-pair spin dynamics. Then, under short time limit, $\Delta P_{(t)}^T$ is obtained as,

$$\Delta P_{(t)}^T \approx (a^2 - b^2)^2 V^2 t^2. \quad (4.21)$$

It is significant to notice that no matter how a and b are combined, the triplet yield benefits from the resonance effect for a singlet born radical pair, as $(a^2 - b^2)^2 > 0$. Moreover, the further a deviates from b , the greater the resonance effect is. $|a| = |b| = 1/\sqrt{2}$, meaning that the eigenstates are evenly populated in the singlet and triplet states, leads to no resonance effect on the reaction yield.

4.1.2 Non-degenerate radical pair

Now we apply the time-dependent perturbation theory to the analysis of a radical pair under an RF field that induces resonance between two eigenstates, $|i\rangle$ and $|j\rangle$, of the unperturbed spin Hamiltonian, $\hat{H}_0$. We assume that there is no degeneracy among the eigenstates. The singlet and triplet projection operators are written,

$$\begin{aligned} \hat{P}^S &= |S\rangle\langle S| \otimes \hat{1}_Z = \sum_n^Z |SI_n\rangle\langle SI_n|, \\ \hat{P}^T &= \sum_{m=+,0,-} |T_m\rangle\langle T_m| \otimes \hat{1}_Z = \sum_n^Z \sum_{m=+,0,-} |T_m I_n\rangle\langle T_m I_n|, \end{aligned} \quad (4.22)$$

where $\hat{1}_Z$ is the identity matrix with Z , the dimension of the nuclear spin space and $|I_n\rangle$ with $n = 1, 2, \dots, Z$ construct an arbitrary orthogonal basis so that

$\sum_n^Z |I_n\rangle\langle I_n| = \hat{1}_Z$. Note that all $|I_n\rangle$ are real for simplicity. Suppose that the radical pair is formed in the singlet state, so that the initial density matrix is

$$\rho_{(0)} = \frac{1}{Z} \hat{P}^S = \frac{1}{Z} \sum_n^Z |SI_n\rangle\langle SI_n|. \quad (4.23)$$

Expanding $|SI_n\rangle$ and $|T_m I_n\rangle$ in the eigenbasis of $\hat{H}_0$ gives

$$\begin{aligned} |SI_n\rangle &= a_i^n |i\rangle + a_j^n |j\rangle + \sum_{k \neq i, j} a_k^n |k\rangle, \\ |T_m I_n\rangle &= b_i^{mn} |i\rangle + b_j^{mn} |j\rangle + \sum_{k \neq i, j} b_k^{mn} |k\rangle. \end{aligned} \quad (4.24)$$

Then, the matrix representations of $\hat{P}^S$ and $\hat{P}^T$ in the eigenbasis of $\hat{H}_0$ are written,

$$\begin{aligned} \hat{P}^S &= \sum_n^Z \begin{pmatrix} |a_i^n|^2 & a_i^n (a_j^n)^* & a_i^n (a_k^n)^* & \cdots \\ a_j^n (a_i^n)^* & |a_j^n|^2 & a_j^n (a_k^n)^* & \cdots \\ a_k^n (a_i^n)^* & a_k^n (a_j^n)^* & |a_k^n|^2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \\ \hat{P}^T &= \sum_n^Z \sum_{m=+,0,-} \begin{pmatrix} |b_i^{mn}|^2 & b_i^{mn} (b_j^{mn})^* & b_i^{mn} (b_k^{mn})^* & \cdots \\ b_j^{mn} (b_i^{mn})^* & |b_j^{mn}|^2 & b_j^{mn} (b_k^{mn})^* & \cdots \\ b_k^{mn} (b_i^{mn})^* & b_k^{mn} (b_j^{mn})^* & |b_k^{mn}|^2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \end{aligned} \quad (4.25)$$

Note that $\hat{P}^S + \hat{P}^T = \hat{1}$, where $\hat{1}$ is the identity matrix including the electron and nuclear spin spaces (i.e. the dimension of $\hat{1}$ is $4Z$). Then, the entries of the matrices in equation (4.25) have following relations:

$$\begin{aligned} \sum_n^Z |a_p^n|^2 + \sum_n^Z \sum_{m=+,0,-} |b_p^{mn}|^2 &= 1, \\ \sum_n^Z a_p^n (a_q^n)^* &= - \sum_n^Z \sum_{m=+,0,-} b_p^{mn} (b_q^{mn})^*. \end{aligned} \quad (4.26)$$

where $p \neq q$. Significantly, note that the radical-pair spin Hamiltonian is symmetric under time reversal, a discrete quantum mechanical symmetry discussed at detail in Section 4.2, so that all the eigenvectors are real (i.e. $(a_p^n)^* = a_p^n$) with

assuming there is no degeneracy in the spin system [85].

Applying a resonant RF field, we write the time-dependent density matrix $\rho(t)$ in the interaction picture,

$$\tilde{\rho}(t) = e^{i\hat{H}_0 t} \rho(t) e^{-i\hat{H}_0 t} = \frac{1}{Z} \sum_n \begin{pmatrix} |\tilde{a}_{i(t)}^n|^2 & \tilde{a}_{i(t)}^n (\tilde{a}_{j(t)}^n)^* & \tilde{a}_{i(t)}^n (\tilde{a}_{k(t)}^n)^* & \cdots \\ \tilde{a}_{j(t)}^n (\tilde{a}_{i(t)}^n)^* & |\tilde{a}_{j(t)}^n|^2 & \tilde{a}_{j(t)}^n (\tilde{a}_{k(t)}^n)^* & \cdots \\ \tilde{a}_{k(t)}^n (\tilde{a}_{i(t)}^n)^* & \tilde{a}_{k(t)}^n (\tilde{a}_{j(t)}^n)^* & |\tilde{a}_{k(t)}^n|^2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (4.27)$$

where $\tilde{a}_{p(t)}^n = e^{i\omega_p t} a_{p(t)}^n$ (ω_p is the eigenvalue of the eigenstate $|p\rangle$ of $\hat{H}_0$). The time-dependent Hamiltonian that accounts for the Zeeman interaction of the electrons with the RF field is represented as

$$\hat{H}'_{(t)} = \hat{H}_{(\mathbf{B}_1, \omega_{\text{rf}}, t)} \otimes \hat{1}_Z = \sum_n \hat{H}_{(\mathbf{B}_1, \omega_{\text{rf}}, t)} \otimes |I_n\rangle \langle I_n|, \quad (4.28)$$

where $\mathbf{B}_1$ characterizes the direction and the amplitude of the fluctuation of the magnetic component of the RF field and ω denotes the oscillating frequency. Note that $\hat{H}'_{(t)}$ does not link states of different nuclear spin configurations (i.e. no such elements, $\hat{H}_{(\mathbf{B}_1, \omega_{\text{rf}}, t)} \otimes |I_n\rangle \langle I_m|$ with $n \neq m$, are contained in $\hat{H}'_{(t)}$). Therefore, transitions between different nuclear spin configurations are not allowed even if the resonance condition has been met (i.e. the resonant RF field causes no transition between $\tilde{a}_{i(t)}^n$ and $\tilde{a}_{j(t)}^m$ with $n \neq m$, whereas it is able to induce transition between $\tilde{a}_{i(t)}^n$ and $\tilde{a}_{j(t)}^n$). $\Delta\omega = \omega_{ji} - \omega_{\text{rf}} = 0$, assuming $\omega_{ji} = \omega_j - \omega_i > 0$, gives rise to the **time-independent** off-diagonal elements of $\hat{H}'_{(t)}$, denoting $\hat{H}'_{(t)}$ in the interaction picture,

$$\langle i | \hat{H}'_{(t)} | j \rangle = \langle j | \hat{H}'_{(t)} | i \rangle = V, \quad (4.29)$$

Ignoring the off-resonant elements of $\hat{H}'_{(t)}$ in the eigenbasis and following the perturbation treatment in equations (4.8 - 4.12) gives

$$\tilde{a}_{i(t)}^n \approx a_i^n - i a_j^n V t, \quad \tilde{a}_{j(t)}^n \approx a_j^n - i a_i^n V t. \quad (4.30)$$

4.1. Non-degenerate resonance

$\rho_{(t)}$ in the Schrödinger picture is obtained using $\rho_{(t)} = e^{-i\hat{H}_0 t} \tilde{\rho}_{(t)} e^{i\hat{H}_0 t}$, so that, remembering equation (4.27), the dynamical populations of $|i\rangle$ and $|j\rangle$ are

$$\rho_{ii(t)} = \frac{A_{ii} + A_{jj} V^2 t^2}{Z(1 + V^2 t^2)}, \quad \rho_{jj(t)} = \frac{A_{jj} + A_{ii} V^2 t^2}{Z(1 + V^2 t^2)}, \quad (4.31)$$

and the dynamical coherences are

$$\begin{aligned} \rho_{ij(t)} &= \frac{A_{ij}(1 + V^2 t^2) + i(A_{ii} - A_{jj})Vt}{Z(1 + V^2 t^2)} e^{-i\omega_{ij}t}, \\ \rho_{ji(t)} &= \frac{A_{ji}(1 + V^2 t^2) + i(A_{jj} - A_{ii})Vt}{Z(1 + V^2 t^2)} e^{-i\omega_{ji}t}, \\ \rho_{ik(t)} &= \frac{A_{ik} - iA_{jk}Vt}{Z\sqrt{1 + V^2 t^2}} e^{-i\omega_{ik}t}, \quad \rho_{ki(t)} = \frac{A_{ki} + iA_{kj}Vt}{Z\sqrt{1 + V^2 t^2}} e^{-i\omega_{ki}t}, \\ \rho_{jk(t)} &= \frac{A_{jk} - iA_{ik}Vt}{Z\sqrt{1 + V^2 t^2}} e^{-i\omega_{jk}t}, \quad \rho_{kj(t)} = \frac{A_{kj} + iA_{ki}Vt}{Z\sqrt{1 + V^2 t^2}} e^{-i\omega_{kj}t}, \end{aligned} \quad (4.32)$$

where

$$\begin{aligned} A_{pp} &= \sum_n^Z |a_p^n|^2 = \langle p | P^S | p \rangle, \\ A_{pq} &= \sum_n^Z a_p^n (a_q^n)^* = \langle p | P^S | q \rangle, \quad \text{for } p \neq q. \end{aligned} \quad (4.33)$$

Note that $A_{pq} = A_{qp}$, as a_q^n is real.

The time-dependent triplet probability is

$$P_{(t)}^T = \mathbf{Tr}\{\hat{P}^T \rho_{(t)}\} = \sum_{p,q}^{4Z} P_{pq}^T \rho_{qp(t)}. \quad (4.34)$$

In the absence of the RF field,

$$P_{pq}^T \rho_{qp(t)} = \frac{1}{Z} \left(\sum_n^Z \sum_{m=+,0,-} b_p^{mn} (b_q^{mn})^* \right) \left(\sum_n^Z a_q^n (a_p^n)^* \right) e^{-i\omega_{qp}t}. \quad (4.35)$$

Using equation (4.26), for $p = q$,

$$P_{pp}^T \rho_{pp(t)} = \frac{1}{Z} \left(1 - \sum_n^Z |a_p^n|^2 \right) \left(\sum_n^Z |a_p^n|^2 \right) = \frac{A_{pp} - A_{pp}^2}{Z}, \quad (4.36)$$

and for $p \neq q$,

$$P_{pq}^T \rho_{qp(t)} = \frac{1}{Z} \left(- \sum_n a_p^n (a_q^n)^* \right) \left(\sum_n a_q^n (a_p^n)^* \right) e^{-i\omega_{qp}t} = -\frac{1}{Z} A_{pq}^2 e^{-i\omega_{qp}t}, \quad (4.37)$$

so that

$$P_{pq}^T \rho_{qp(t)} + P_{qp}^T \rho_{pq(t)} = -\frac{2}{Z} A_{pq}^2 \cos(\omega_{pq}t). \quad (4.38)$$

Recalling equation (4.32), the application of the resonant RF field gives

$$\begin{aligned} P_{ij}^T \rho_{ji(t)} + P_{ji}^T \rho_{ij(t)} &= -\frac{2}{Z} A_{ij}^2 \cos(\omega_{ij}t) + \frac{1}{Z} \sin(2Vt) \sin(\omega_{ji}t) (A_{ii} - A_{jj}) A_{ij}, \\ P_{ik}^T \rho_{ki(t)} + P_{ki}^T \rho_{ik(t)} &= -\frac{2}{Z} A_{ik}^2 \cos(\omega_{ik}t) + \frac{1}{Z} \sin(2Vt) \sin(\omega_{ik}t) A_{ik} A_{jk}, \\ P_{jk}^T \rho_{kj(t)} + P_{kj}^T \rho_{jk(t)} &= -\frac{2}{Z} A_{jk}^2 \cos(\omega_{jk}t) + \frac{1}{Z} \sin(2Vt) \sin(\omega_{jk}t) A_{jk} A_{ik}, \end{aligned} \quad (4.39)$$

where we have adopted the treatment in equations (4.14 - 4.18). Compared with equation (4.38), the additional oscillatory terms in equation (4.39) would be averaged out when calculating the yield of reaction products because of the zero-quantum coherence term, e.g. $\sin(\omega_{ji}t)$ ($\omega_{ij} \gg k$). Then, the resonance effect focuses on the transition term obtained as

$$\Delta(P_{ii}^T \rho_{ii(t)} + P_{jj}^T \rho_{jj(t)}) = \frac{1}{Z} (A_{ii} - A_{jj})^2 \sin^2(Vt), \quad (4.40)$$

according to equation (4.31). Under short-time limit $V^2 t^2 \ll 1$, the change in the time-dependent triplet probability brought about by the resonant RF field is written

$$\Delta P_{(t)}^T = \frac{1}{Z} |\langle i | \hat{P}^S | i \rangle - \langle j | \hat{P}^S | j \rangle|^2 |\langle i | \hat{H}'_{(t)} | j \rangle|^2 t^2, \quad (4.41)$$

where $|\langle i | \hat{H}'_{(t)} | j \rangle|^2$ quantifies the transition intensity [109]. Note that the energy levels of the spin Hamiltonian of a radical pair are still sufficiently discrete, so that it is not appropriate to adopt the concept of “density of states”¹ for continuum

¹Number of continuum states divided by dE in the infinitesimally small energy interval E to $E + dE$.

states in Fermi's golden rule. Thus, the expression of the **squared** population difference, $|\langle i|\hat{P}^S|i\rangle - \langle j|\hat{P}^S|j\rangle|^2$, must be included in $\Delta P_{(t)}^T$. Notice that $\Delta P_{(t)}^T$ is positive, so that the triplet yield would always benefit (so the drop of the singlet yield) from the resonance effect.

4.2 Significance of degeneracy

The resonance effect on a radical pair is closely related to the difference in the initial populations of the eigenstates (equation (4.41)). However, it is very strange that the energy eigenstates of the radical pair are all identically populated for an initial singlet state when there is an odd number of hyperfine-coupled hydrogens in either one or both radicals,

$$\langle v|\rho_{(0)}|v\rangle = \frac{1}{Z}\langle v|\hat{P}^S|v\rangle = \frac{1}{4Z}, \quad (4.42)$$

where $|v\rangle$ is an arbitrary eigenstate of the radical-pair spin Hamiltonian. This is not related to the number of hyperfine-coupled nitrogens. Equation (4.42) does not apply when there is an even number of hyperfine-coupled hydrogens in both radicals. The uniformly populated eigenstates should prevent a resonant RF field causing any appreciable change in the reaction yields even though the resonance condition has been met. In this way, the resonance effect seems to be closely related to the number of hyperfine-coupled hydrogens included in the spin system. However, a previous computational study [45] clearly shows that resonance induced by an RF field remarkably changes the singlet yield of a one-proton radical pair (i.e. one hyperfine-coupled hydrogen is included). There must be particular physics behind this.

4.2.1 Kramers degeneracy

We firstly investigate the origin of equation (4.42). Write the singlet projection operator in terms of the electron spin operators,

$$\hat{P}^S = \frac{1}{4}\hat{\mathbb{1}} - \sum_{\alpha=x,y,z} \hat{S}_{1\alpha}\hat{S}_{2\alpha}. \quad (4.43)$$

Ignoring the inter-radical interactions, an eigenstate of the radical pair can be represented as the tensor product of two eigenstates of the two radicals,

$$|v\rangle = |v^1\rangle \otimes |v^2\rangle. \quad (4.44)$$

Then, equation (4.42) is equivalent to

$$\langle v^i | \hat{S}_{i\alpha} | v^i \rangle = 0, \quad (4.45)$$

if there is an odd number of hyperfine-coupled hydrogens in radical i . The origin of equation (4.45) is considered associated to a discrete symmetry in quantum mechanics, time-reversal symmetry. Time-reversal is more precisely termed as reversal of motion [85]. The operation of time-reversal is characterized by the operator $\hat{\Theta}$, and a state $|\psi\rangle$ under time-reversal is denoted by $|\psi^T\rangle$,

$$|\psi^T\rangle = \hat{\Theta}|\psi\rangle. \quad (4.46)$$

A significant identity is

$$\langle \varphi | \hat{O} | \psi \rangle = \langle \psi^T | \hat{\Theta} \hat{O}^\dagger \hat{\Theta}^{-1} | \varphi^T \rangle, \quad (4.47)$$

where $\hat{O}$ is a generic linear operator. Spin operators are odd under time reversal,

$$\hat{\Theta} \hat{S}_\alpha \hat{\Theta}^{-1} = -\hat{S}_\alpha \text{ for } \alpha = x, y, z, \quad (4.48)$$

which is required by their fundamental commutation relations as in equation (2.2) [85]. The expression of $\hat{\Theta}$ for a spin system is,

$$\hat{\Theta} = \eta e^{-i\pi \hat{S}_y} \hat{K}, \quad (4.49)$$

where η stands for an arbitrary phase, a complex number of modulus unity $|\eta|^2 = 1$ and $\hat{K}$ is the complex conjugate operator. Taking spin-1/2 as an example: all the matrix elements of $\hat{S}_x$ and $\hat{S}_z$ are real, so that $\hat{\Theta}$ is equivalent to a rotation operator $\mathcal{D}_{(\mathbf{y}, \pi)}$ (rotation around the y -axis by π), and for $\hat{S}_y$, $\hat{\Theta}$ is reduced to $\hat{K}$. Thus, equation (4.49) is consistent with equation (4.48). Furthermore, applying $\hat{\Theta}$ twice gives the 2π rotation operator:

$$\hat{\Theta}^2 = \eta e^{-i\pi\hat{S}_y} \hat{K} \eta e^{-i\pi\hat{S}_y} \hat{K} = \eta\eta^* e^{-i\pi\hat{S}_y} e^{+i\pi(\hat{S}_y)^*} \hat{K}^2 = e^{-i2\pi\hat{S}_y} = \mathcal{D}_{(\mathbf{y}, 2\pi)}, \quad (4.50)$$

where $\hat{K}^2 = \hat{\mathbb{1}}$. The radical-pair spin Hamiltonian in the absence of any external magnetic field consists of the hyperfine interactions of the unpaired electrons with the nuclear spins:

$$\hat{H}_0 = \sum_{i=1,2} \hat{H}_{0i} = \sum_{i=1,2} \sum_k \hat{\mathbf{S}}_i \cdot \mathbf{A}_{ik} \cdot \hat{\mathbf{I}}_{ik}, \quad (4.51)$$

where $\hat{H}_{0i}$ denotes the spin Hamiltonian of radical i , $\hat{\mathbf{S}}_i$ and $\hat{\mathbf{I}}_{ik}$ denote the electron spin and the k -th nuclear spin in radical i respectively, and $\mathbf{A}_{ik}$ is the corresponding hyperfine tensor. Inter-radical interactions have been ignored here. One finds that $\hat{H}_{0i}$ (so $\hat{H}_0$) is symmetric under time reversal, $\hat{\Theta} \hat{H}_{0i} \hat{\Theta}^{-1} = \hat{H}_{0i}$ (i.e. $\hat{\Theta}$ commutes with $\hat{H}_{0i}$), because of $\hat{\Theta} \hat{S}_{i\alpha} \hat{I}_{ik\beta} \hat{\Theta}^{-1} = (-\hat{S}_{i\alpha})(-\hat{I}_{ik\beta}) = \hat{S}_{i\alpha} \hat{I}_{ik\beta}$ for $\alpha, \beta = x, y, z$. Then, the time-reversed $|v^i\rangle$ is also an eigenstate of $\hat{H}_{0i}$ with the same eigenvalue ω^i ,

$$\hat{H}_{0i} (\hat{\Theta}|v^i\rangle) = \hat{\Theta} \hat{H}_{0i} |v^i\rangle = \omega^i \hat{\Theta}|v^i\rangle. \quad (4.52)$$

Importantly, note that $\hat{\Theta}|v^i\rangle$ is not necessarily a degenerate state of $|v^i\rangle$, as they could denote the same state (i.e. at most differing by a phase factor),

$$\hat{\Theta}|v^i\rangle = e^{i\zeta}|v^i\rangle. \quad (4.53)$$

Applying $\hat{\Theta}^2$ can determine the identity of $\hat{\Theta}|v^i\rangle$, according to equation (2.43),

$$\hat{\Theta}^2 = \mathcal{D}_{(\mathbf{y}, 2\pi)} = (-1)^{N_{\text{half}}} \hat{\mathbb{1}}, \quad (4.54)$$

where N_{half} denotes the number of half-integer spin particles in the spin system. A radical including an odd number of hyperfine-coupled hydrogens and the unpaired electron is a system of even number of half-integer spin particles, so that $\hat{\Theta}^2 = \hat{1}$. Then, $\hat{\Theta}|v^i\rangle$ and $|v^i\rangle$ must denote the same state if there is no source of degeneracy from the symmetry of the hyperfine tensors (e.g. axiality $A_{xx} = A_{yy} \neq A_{zz}$), since

$$\hat{\Theta}^2|v^i\rangle = \hat{\Theta}\hat{\Theta}|v^i\rangle = e^{-i\zeta}e^{i\zeta}|v^i\rangle = |v^i\rangle. \quad (4.55)$$

This gives rise to the quenching of the spin angular momentum of radical i using equation (4.47),

$$\begin{aligned} \langle v^i|\hat{S}_{i\alpha}|v^i\rangle &= \langle (v^i)^T|\hat{\Theta}\hat{S}_{i\alpha}\hat{\Theta}^{-1}|(v^i)^T\rangle \\ &= \langle v^i|e^{-i\zeta}(-\hat{S}_{i\alpha})e^{i\zeta}|v^i\rangle \\ &= -\langle v^i|\hat{S}_{i\alpha}|v^i\rangle \\ &= 0. \end{aligned} \quad (4.56)$$

This explains the strange phenomenon in equation (4.42) for an odd number of hyperfine-coupled hydrogens. By contrast, equation (4.53) can never apply for a radical with an even number of hyperfine-coupled hydrogens, since $\hat{\Theta}^2 = -\hat{1}$. This means that $\hat{\Theta}|v^i\rangle$ must be a degenerate state of $|v^i\rangle$ (i.e. $\hat{\Theta}|v^i\rangle$ and $|v^i\rangle$ denote **different** states), even if no degeneracy is expected from the hyperfine tensor (i.e. $A_{xx} \neq A_{yy} \neq A_{zz}$). Such degeneracy required by time-reversal symmetry is the so-called Kramers degeneracy, which allows the non-zero spin angular momentum,

$$\langle v^i|\hat{S}_{i\alpha}|v^i\rangle = -\langle (v^i)^T|\hat{S}_{i\alpha}|(v^i)^T\rangle \neq 0. \quad (4.57)$$

Therefore, the eigenstates are not necessarily identically populated in the initial singlet state, if there are even numbers of hyperfine-coupled hydrogens in both radicals.

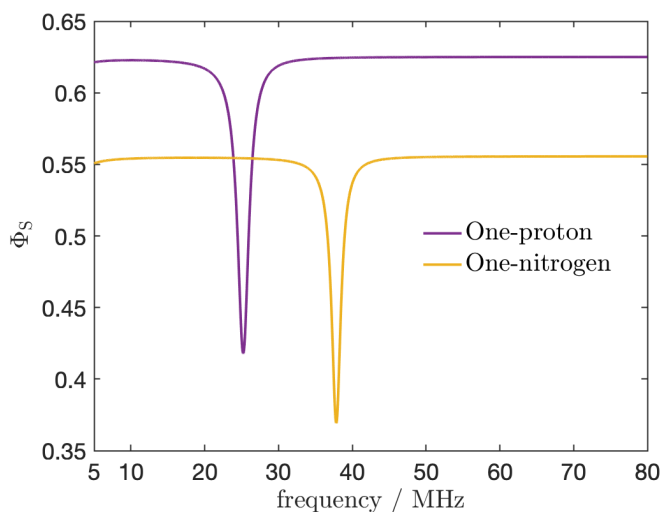


Figure 4.2: Singlet yield (calculated by γ -COMPUTE) as a function of the frequency of a 50 μ T RF field, for the one-proton or one-nitrogen radical pair. The hyperfine tensor is isotropic: $A_{xx} = A_{yy} = A_{zz} = 0.9$ mT.

4.2.2 Degenerate resonance effect

The dependence of the resonance effect of an RF field on the number of the hyperfine-coupled hydrogens is counter-intuitive, though it is explained by time-reversal symmetry. It is difficult to accept that a radical pair would stop showing a resonance effect if one more hydrogen was taken into account. Simulations² for two (one-proton and one-nitrogen) toy radical pairs are illustrated in Figure 4.2. The applied 50 μ T RF field at the resonant frequency (25.3 MHz for the one-proton radical pair and 37.8 MHz for the one-nitrogen radical pair) produces efficient transitions between energy eigenstates, which remarkably increases the efficiency of the singlet-triplet interconversion. Therefore, the singlet yield for the singlet-born radical pair drops at resonant frequencies (see the spikes in Figure 4.2). Whereas in the off-resonance region, an RF field does not have a noticeable effect on the radical-pair spin dynamics. Degeneracies induced by the symmetry of the hyperfine interactions, which has been omitted in the analysis in Section

² γ -COMPUTE is adopted for the calculation of the reaction yield. See C. T. Rodgers, DPhil Thesis, for detailed description for γ -COMPUTE [120].

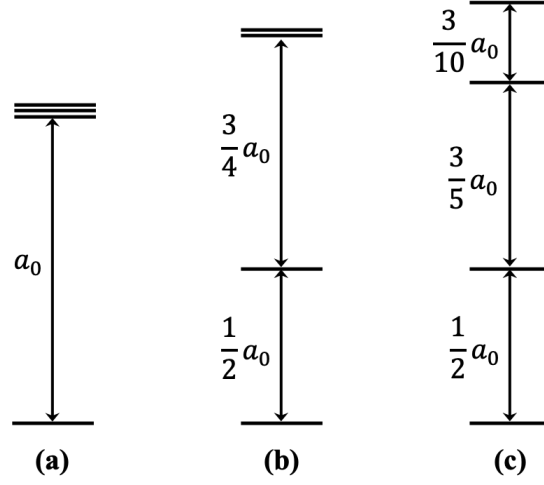


Figure 4.3: Zero-field energy levels for the radical with one hyperfine-coupled proton. The hyperfine parameters are characterized by equation (4.58). (a) Three-fold degeneracy is shown when $\alpha = \beta = 0$. (b) Two-fold degeneracy is shown when $\alpha = 0.5$ and $\beta = 0$. (c) No degeneracy is shown when $\alpha = 0.5$ and $\beta = 0.6$.

4.1, plays an important role in resonance effects on radical-pair spin dynamics. In order to present the significance of the degeneracy, we vary the parameters of the hyperfine tensor for the one-proton radical pair. The three principal elements of the hyperfine tensor are

$$A_{xx} = a_0(1 - \alpha)(1 - \beta), \quad A_{yy} = a_0(1 - \alpha)(1 + \beta), \quad A_{zz} = a_0(1 + 2\alpha), \quad (4.58)$$

where α and β characterize the axially and rhombicity of the hyperfine tensor respectively. α and β determine the degeneracy of the eigenstates for the radical with the hydrogen (note that the singlet and triplet states of the hydrogen-included radical refer to the electron and hydrogen spins): (1) $\alpha = \beta = 0$: the eigenstates consist of one singlet state and three degenerate triplet states (three-fold degeneracy in Figure 4.3(a)); (2) $\alpha \neq 0$ and $\beta = 0$: the eigenstates are the same as in (1), but only two triplet states are degenerate (two-fold degeneracy in Figure 4.3(b)); (3) $\beta \neq 0$ with an arbitrary α : no degeneracy emerges among the eigenstates (in Figure 4.3(c)). The quantum yield of the electronic singlet product state $\Phi_{S(B_1, \mathbf{n}_1, \omega_{rf})}$ is calculated as a function of the direction, denoted by a unit vector

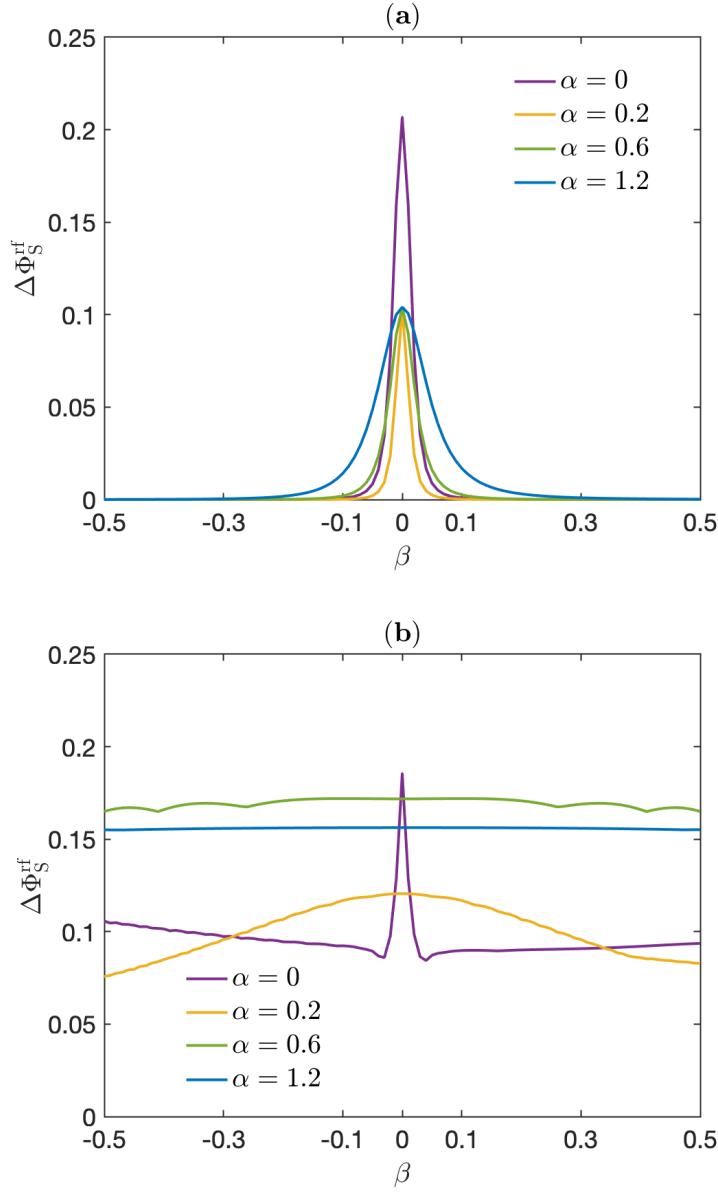


Figure 4.4: $\Delta\Phi_S^{\text{rf}}$ is calculated (using γ -COMPUTE) as a function of β , with $\alpha = 0, 0.2, 0.6$ and 1.2 , for (a) one-proton radical pair and for (b) one-nitrogen radical pair.

$\mathbf{n}_1$, and the frequency ω_{rf} of the RF field. ω_{rf} ranges in 5-80 MHz. $\mathbf{n}_1$ is represented by the polar angle θ and azimuthal angle ϕ which characterize the angle of the oscillation direction of the magnetic component of the RF field relative to internal hyperfine axes. B_1 is the oscillation amplitude (here $B_1 = 50 \mu\text{T}$). In the absence of any external magnetic field, the singlet yield is denoted by $\Phi_{\text{S}(0)}$. The resonance effect is characterized by the difference between $\Phi_{\text{S}(0)}$ and the minimum singlet

yield, $\min\{\Phi_{S(B_1, \mathbf{n}_1, \omega_{\text{rf}})}\}$, for all frequencies and all directions of the applied RF field: $\Delta\Phi_{\text{S}}^{\text{rf}} = \Phi_{S(0)} - \min\{\Phi_{S(B_1, \mathbf{n}_1, \omega_{\text{rf}})}\}$. In Figure 4.4(a), $\alpha = \beta = 0$ (so the three-fold degeneracy) gives rise to the largest resonance-induced change in the singlet yield. The resonance effect can still be seen when $\alpha \neq 0$ and $\beta = 0$, though $\Delta\Phi_{\text{S}}^{\text{rf}}$ becomes nearly 50% smaller, given that the degeneracy has reduced to two-fold. Strictly speaking, $\beta \neq 0$ removes the degeneracy of the radical carrying the hydrogen, but β not far from zero preserves the near degeneracy in this radical, which still allows the resonance effect (see the width of $\Delta\Phi_{\text{S}}^{\text{rf}}$ spectra at the vicinity of $\beta = 0$). Nevertheless, the completely non-degenerate radical pair, as β deviates further from zero, is **indeed** unable to show any resonance effect on $\Delta\Phi_{\text{S}}^{\text{rf}}$, as is expected by equations (4.41) and (4.42). By contrast, the singlet yield of a one-nitrogen radical pair is always remarkably affected by the resonant RF field no matter how α and β are assigned (Figure 4.4(b)), as a result of Kramers degeneracy certainly given by time-reversal symmetry. Therefore, we conclude that it is the (near) degeneracy in the radical pair that is necessary for a resonant RF field to modulate the reaction yield in the absence of an external static field. An odd number of hyperfine-coupled hydrogens (i.e. no Kramers degeneracy) does not signify the erasing of the resonance effect if there exists some symmetry in the hyperfine interactions, e.g. axially.

4.3 Radiofrequency polarization

In a previous study [45], both the experimental and simulated zero-field EPR spectra exhibit the resonance effect on the singlet yield and the polarization of the oscillating RF field (i.e. right-circularly (CP+) or left-circularly (CP-) polarized) does not give rise to any difference to the change in the singlet yield brought by the RF field. As is shown in Figure 4.5(a) and (b), the resonance effect on the singlet yield by the CP+ or CP- RF field is indeed identical for

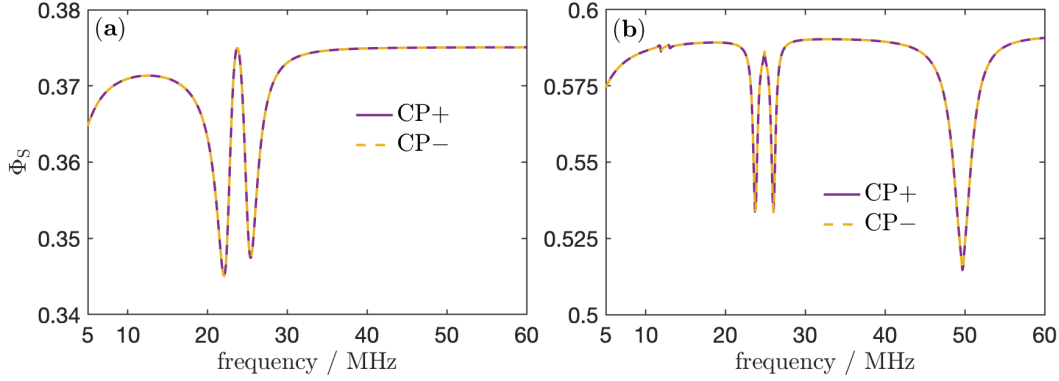


Figure 4.5: Singlet yield for the (a) one-proton radical pair and (b) one-nitrogen radical pair, as a function of the frequency for the CP+ or CP– RF field ($B_1 = 50 \mu\text{T}$). The hyperfine tensor: $A_{xx} = A_{yy} = -0.1 \text{ mT}$ and $A_{zz} = 1.7 \text{ mT}$. The radical pair lifetime is $1 \mu\text{s}$.

either a one-proton or one-nitrogen radical pair. Such **equal** resonance effect of the CP+ and CP– field is peculiar at first glance, since conventionally in the presence of applied static field B_0 ($B_0 \gg B_1$), if the CP+ field rotates around B_0 with Larmor frequency to produce resonance effect, then the CP– field would be off-resonance. We suppose that the equivalence between a resonant CP+ and CP– field fundamentally originates in the time-reversal symmetry of the zero-field radical pair (without a static field to break this symmetry). Firstly, consider an electron in an static magnetic field directed parallel to the z -axis. The electron spin originally along the z -axis will spiral into the x, y -plane under a CP+ RF field oscillating at the Larmor frequency. If the static field is directed anti-parallel to the z -axis, then the RF field needs to be CP– polarized so as to produce the resonance. The matrix representations of the Hamiltonians, describing the interactions of the electron with the static field and the corresponding resonant RF field, are written,

$$\hat{H}_0^+ = \omega_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{H}_{(t)}'^+ = \omega_1 \begin{pmatrix} 0 & e^{-i\omega_{\text{rf}}^+ t} \\ e^{+i\omega_{\text{rf}}^+ t} & 0 \end{pmatrix}; \quad (4.59a)$$

$$\hat{H}_0^- = -\omega_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{H}_{(t)}'^- = \omega_1 \begin{pmatrix} 0 & e^{-i\omega_{\text{rf}}^- t} \\ e^{+i\omega_{\text{rf}}^- t} & 0 \end{pmatrix}, \quad (4.59b)$$

where $\hat{H}_0^+$ and $\hat{H}_0^-$ respectively indicate that the static field is directed parallel and anti-parallel to the z -axis ($\omega_0 > 0$), $\hat{H}_{(t)}^+$ and $\hat{H}_{(t)}^-$ stand for the CP+ and CP− RF field (here $\omega_{\text{rf}}^+ > 0$, $\omega_{\text{rf}}^- < 0$ and $\omega_{\text{rf}}^+ = -\omega_{\text{rf}}^-$). One will immediately find that $\hat{H}_0^-$ is $\hat{H}_0^+$ under time reversal operation (i.e. $\hat{\Theta} \hat{H}_0^+ \hat{\Theta}^{-1} = \hat{H}_0^-$). Then, a bold speculation is that if a CP+ RF field can cause resonance for a spin system, the CP− RF field at the same frequency will cause resonance for the time reversed system. In terms of a zero-field radical pair, which is symmetric under time reversal (equation (4.51)), the CP+ and CP− RF fields are expected to have the same resonance effect on the spin dynamics.

Although the analogy with the single electron case is truly inspiring, stringent theoretical evidence for the time-reversal induced CP+/CP− equivalence will be given. Consider two eigenstates of radical 1, $|\alpha\rangle$ and $|\beta\rangle$ with the corresponding energy eigenvalues ω_α and ω_β . Assume that both radicals have an even number of hyperfine-coupled hydrogens, so that there is no need to worry about the awkwardness of uniformly populated eigenstates. Suppose the applied CP+ RF field meets the resonance condition. The Hamiltonian of the Zeeman interaction of the electron with the CP+ RF field is written,

$$\hat{H}_{1(t)}^+ = \hat{H}_{(t)}'^+ \otimes \hat{1}_{Z_1}, \quad (4.60)$$

where $\hat{H}_{(t)}'^+$ is as in equation (4.59a) and $\hat{1}_{Z_1}$ denotes the identity matrix with the nuclear spin dimension of radical 1. Write $|\alpha\rangle$ in the basis of individual spins of the electron and nuclei in radical 1, where N_1 nuclear spins are included:

$$|\alpha\rangle = \sum_{s, m} \sum_{m_e, m_n, \{\gamma\}} |s_e, s_n^{\{\gamma\}}; m_e, m_n\rangle C_{m_e, m_n}^{s, m} C_{s, m}^\alpha, \quad (4.61)$$

where the subscript e denotes the electron and n denotes the entire configuration of nuclear spins, $C_{m_e, m_n}^{s, m} = \langle s_e, s_n^{\{\gamma\}}; m_e, m_n | s; m \rangle$ is the Clebsch-Gordan coefficient,

4.3. Radiofrequency polarization

in which $|s; m\rangle$ denotes an eigenstate of the total spin operator for radical 1, with

$$m = m_e + m_n, \quad (4.62a)$$

$$|s_e - s_n^{\{\gamma\}}| \leq s \leq s_e + s_n^{\{\gamma\}} \quad (4.62b)$$

$C_{s,m}^\alpha = \langle s; m | \alpha \rangle$ is not necessarily real as a result of the intrinsic Kramers degeneracy [85]. Similarly for $|\beta\rangle$:

$$|\beta\rangle = \sum_{s', m'} \sum_{m'_e, m'_n, \{\gamma'\}} |s_e, s_n^{\{\gamma'\}}; m'_e, m'_n\rangle C_{m'_e, m'_n}^{s', m'} C_{s', m'}^\beta. \quad (4.63)$$

The intensity of the transition between $|\alpha\rangle$ and $|\beta\rangle$, $|\mathcal{I}_{\alpha, \beta}^+|^2$, is calculated following that in equation (4.41):

$$\begin{aligned} \mathcal{I}_{\alpha, \beta}^+ &= \langle \beta | \hat{H}_{1(t)}^+ | \alpha \rangle \\ &= \sum_{s', m'} \sum_{s, m} \sum_{m'_e, m'_n, \{\gamma'\}} \langle s_e; m'_e | \hat{H}_{(t)}^+ | s_e; m_e \rangle \times \\ &\quad \delta_{(m_n, m'_n)} \delta_{(\{\gamma\}, \{\gamma'\})} C_{m'_e, m'_n}^{s', m'} C_{m_e, m_n}^{s, m} (C_{s', m'}^\beta)^* C_{s, m}^\alpha e^{i(\omega_\beta - \omega_\alpha)t}, \end{aligned} \quad (4.64)$$

where $\hat{H}_{1(t)}^+$ denotes $\hat{H}_{1(t)}^+$ in the interaction picture, and $|s_e, s_n^{\{\gamma\}}; m_e, m_n\rangle = |s_e; m_e\rangle \otimes |s_n^{\{\gamma\}}; m_n\rangle$ is used. Noticing that $|s_n^{\{\gamma\}}; m_n\rangle$ constructs an orthogonal basis, so that Kronecker δ function emerges as $\langle s_n^{\{\gamma'\}}; m'_n | \hat{1}_{Z_1} | s_n^{\{\gamma\}}; m_n \rangle = \delta_{(m_n, m'_n)} \delta_{(\{\gamma\}, \{\gamma'\})}$. The resonance condition is satisfied by $\omega_{\text{rf}}^+ = \omega_\beta - \omega_\alpha$, which requires

$$m'_e = \frac{1}{2}, \quad m_e = -\frac{1}{2} \quad (4.65)$$

to cancel the oscillatory term $e^{i(\omega_\beta - \omega_\alpha)t}$ so as to preserve the time-independence of $\mathcal{I}_{\alpha, \beta}^+$. Combining equations (4.62(a)) and (4.65) and $\delta_{(m_n, m'_n)}$ gives

$$m' = m + 1. \quad (4.66)$$

Thus, $\mathcal{I}_{\alpha, \beta}^+$ is simplified as

$$\mathcal{I}_{\alpha, \beta}^+ = \sum_{s', s, m} \sum_{m_n, \{\gamma\}} \omega_1 C_{\frac{1}{2}, m_n}^{s', m+1} C_{-\frac{1}{2}, m_n}^{s, m} (C_{s', m+1}^\beta)^* C_{s, m}^\alpha. \quad (4.67)$$

Swapping the applied CP+ field for a CP− field gives

$$\hat{H}_{1(t)}^- = \hat{H}_{(t)}'^- \otimes \hat{1}_{Z_i}, \quad (4.68)$$

in which $\omega_{\text{rf}}^- = -\omega_{\text{rf}}^+ = \omega_\alpha - \omega_\beta$. Then, the resonance between $|\alpha\rangle$ and $|\beta\rangle$ requires

$$m_e' = -\frac{1}{2}, \quad m_e = \frac{1}{2}, \quad (4.69)$$

to produce a time-independent $\mathcal{I}_{\alpha,\beta}^-$. Then, $\mathcal{I}_{\alpha,\beta}^-$ is obtained as

$$\mathcal{I}_{\alpha,\beta}^- = \langle \beta | \hat{H}_{1(t)}^- | \alpha \rangle = \sum_{s', s, m} \sum_{m_n, \{\gamma\}} \omega_1 C_{-\frac{1}{2}, m_n}^{s', m} C_{\frac{1}{2}, m_n}^{s, m+1} (C_{s', m}^\beta)^* C_{s, m+1}^\alpha. \quad (4.70)$$

The summations over s and s' have the same limit as in equation (4.62b), which allows the exchange of s and s' in equation (4.70):

$$\mathcal{I}_{\alpha,\beta}^- = \sum_{s', s, m} \sum_{m_n, \{\gamma\}} \omega_1 C_{\frac{1}{2}, m_n}^{s', m+1} C_{-\frac{1}{2}, m_n}^{s, m} (C_{s, m}^\beta)^* C_{s', m+1}^\alpha. \quad (4.71)$$

$|\mathcal{I}_{\alpha,\beta}^+|^2$ is not necessarily equal to $|\mathcal{I}_{\alpha,\beta}^-|^2$, meaning that CP+ and CP− RF fields could have different transition intensities between $|\alpha\rangle$ and $|\beta\rangle$. Then, why is the CP+/CP− equivalence? Time-reversal symmetry, again, plays a critical role in this puzzle. Instead of looking into the transition between $|\alpha\rangle$ and $|\beta\rangle$, we focus on the transition between $|\alpha^\mathcal{T}\rangle$ and $|\beta^\mathcal{T}\rangle$ arising from the application of the CP− RF field. Theorem [121]: for a half-integer spin system that is symmetric under time-reversal:

$$\hat{\Theta}|s; m\rangle = (-1)^{s-m}|s; -m\rangle, \quad (4.72)$$

where $|s; m\rangle$ is an eigenstate of the total spin operator. Then, $|\alpha^\mathcal{T}\rangle$ is written,

$$\begin{aligned} |\alpha^\mathcal{T}\rangle &= \sum_{s, m} \hat{\Theta} C_{s, m}^\alpha |s; m\rangle \\ &= \sum_{s, m} \sum_{m_e, m_n, \{\gamma\}} (-1)^{s-m} |s_e, s_n^{\{\gamma\}}; -m_e, -m_n\rangle C_{-m_e, -m_n}^{s, -m} (C_{s, m}^\alpha)^* \\ &= \sum_{s, m} \sum_{m_e, m_n, \{\gamma\}} (-1)^{s_e + s_n^{\{\gamma\}} - m} |s_e, s_n^{\{\gamma\}}; -m_e, -m_n\rangle C_{m_e, m_n}^{s, m} (C_{s, m}^\alpha)^*, \end{aligned} \quad (4.73)$$

4.3. Radiofrequency polarization

where the symmetry property [121] of the Clebsch-Gordan coefficient is used to give $C_{-m_e, -m_n}^{s, -m} = (-1)^{s_e + s_n^{\{\gamma\}} - s} C_{m_e, m_n}^{s, m}$. Similarly for $|\beta^T\rangle$,

$$|\beta^T\rangle = \sum_{s', m'} \sum_{m'_e, m'_n, \{\gamma'\}} (-1)^{s_e + s_n^{\{\gamma'\}} - m'} |s_e, s_n^{\{\gamma'\}}; -m'_e, -m'_n\rangle C_{m'_e, m'_n}^{s', m'} (C_{s', m'}^\beta)^*. \quad (4.74)$$

Thus, $\mathcal{I}_{\alpha^T, \beta^T}^-$ is obtained as

$$\begin{aligned} \mathcal{I}_{\alpha^T, \beta^T}^- &= \langle \beta^T | \hat{H}_{1(t)}^- | \alpha^T \rangle \\ &= \sum_{s', m'} \sum_{s, m} \sum_{m'_e, m'_n, m_n} (-1)^{2(s_e + s_n^{\{\gamma\}}) - m' - m} \langle s_e; -m'_e | \hat{H}_{(t)}^- | s_e; -m_e \rangle \times \\ &\quad \delta_{(-m_n, -m'_n)} \delta_{(\{\gamma\}, \{\gamma'\})} C_{m'_e, m'_n}^{s', m'} C_{m_e, m_n}^{s, m} C_{s', m'}^\beta (C_{s, m}^\alpha)^* e^{i(\omega_\beta - \omega_\alpha)t}. \end{aligned} \quad (4.75)$$

Remembering $\omega_{\text{rf}}^- = \omega_\alpha - \omega_\beta$ and $\hat{H}_{(t)}^-$ in equation (4.59b),

$$-m'_e = -\frac{1}{2}, \quad -m_e = \frac{1}{2} \quad (\text{so that } m'_e = \frac{1}{2}, \quad m_e = -\frac{1}{2}), \quad (4.76)$$

to cancel $e^{i(\omega_\beta - \omega_\alpha)t}$ in equation (4.75). $\delta_{(-m_n, -m'_n)}$ gives $m_n = m'_n$, so that $m' = m + 1$. Moreover,

$$(-1)^{2(s_e + s_n^{\{\gamma\}}) - m' - m} = (-1)^{2(s_e + s_n^{\{\gamma\}}) - 2m - 1} = -1, \quad (4.77)$$

which is attributed to the half-integer total spin of the radical. Then, $\mathcal{I}_{\alpha^T, \beta^T}^-$ in equation (4.75) is simplified as

$$\mathcal{I}_{\alpha^T, \beta^T}^- = - \sum_{s', s, m} \sum_{m_n, \{\gamma\}} \omega_1 C_{\frac{1}{2}, m_n}^{s', m+1} C_{-\frac{1}{2}, m_n}^{s, m} ((C_{s', m+1}^\beta)^* C_{s, m}^\alpha)^*. \quad (4.78)$$

Surprisingly, in comparison with $\mathcal{I}_{\alpha, \beta}^+$ in equation (4.67), the two transition intensities are equal:

$$|\mathcal{I}_{\alpha, \beta}^+|^2 = |\mathcal{I}_{\alpha^T, \beta^T}^-|^2. \quad (4.79)$$

Besides, the population of $|\alpha, v^2\rangle$ in the initial singlet state of the radical pair is equal to that of the time-reversed one, $|\alpha^T, (v^2)^T\rangle$:

$$\langle \alpha, v^2 | \hat{P}^S | \alpha, v^2 \rangle = \langle \alpha^T, (v^2)^T | \hat{\Theta} \hat{P}^S \hat{\Theta}^{-1} | \alpha^T, (v^2)^T \rangle = \langle \alpha^T, (v^2)^T | \hat{P}^S | \alpha^T, (v^2)^T \rangle, \quad (4.80)$$

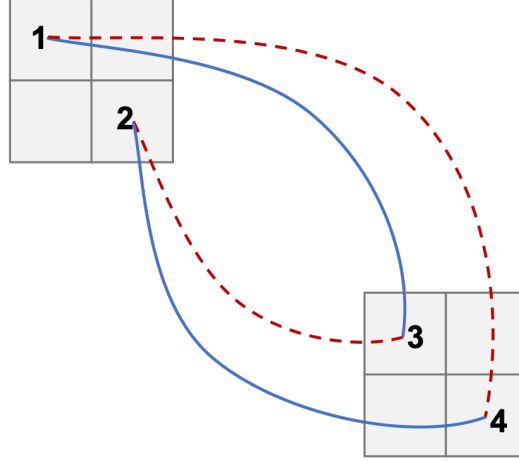


Figure 4.6: Scheme for the resonance between two degenerate subspaces. The pair of degenerate eigenstates in each subspace are time-reversed to each other (i.e. $\hat{\Theta}|1\rangle = |2\rangle$, $\hat{\Theta}|3\rangle = |4\rangle$). The traces, linking the two degenerate subspaces, indicate the equivalence of the transitions induced by a CP+ or a CP– RF field. For instance, blue solid traces: the transition between $|1\rangle$ and $|3\rangle$ turned on by a CP+ RF field is equivalent to that between $|2\rangle$ and $|4\rangle$ induced by a CP– RF field.

where $|\alpha, v^2\rangle = |\alpha\rangle \otimes |v^2\rangle$ in which $|v^2\rangle$ is an arbitrary eigenstate of radical 2, and $|\alpha^\mathcal{T}, (v^2)^\mathcal{T}\rangle = \hat{\Theta}|\alpha, v^2\rangle$. Note that we have used the symmetry of $\hat{P}^S$ under time reversal (see equations (4.43) and (4.48)). Same for $|\beta, v^j\rangle$:

$$\langle\beta, v^2|\hat{P}^S|\beta, v^2\rangle = \langle\beta^\mathcal{T}, (v^2)^\mathcal{T}|\hat{P}^S|\beta^\mathcal{T}, (v^2)^\mathcal{T}\rangle. \quad (4.81)$$

Hence,

$$\begin{aligned} & |\langle\alpha, v^2|\hat{P}^S|\alpha, v^2\rangle - \langle\beta, v^2|\hat{P}^S|\beta, v^2\rangle|^2 \\ &= |\langle\alpha^\mathcal{T}, (v^2)^\mathcal{T}|\hat{P}^S|\alpha^\mathcal{T}, (v^2)^\mathcal{T}\rangle - \langle\beta^\mathcal{T}, (v^2)^\mathcal{T}|\hat{P}^S|\beta^\mathcal{T}, (v^2)^\mathcal{T}\rangle|^2. \end{aligned} \quad (4.82)$$

Combining equations (4.41), (4.79) and (4.82), we conclude that as long as a resonant CP+ RF field induces the transition between two eigenstates of the radical pair to affect the reaction yield, the CP– RF field at the same oscillating frequency can produce the identical effect on the reaction yield through turning on the equal transition between the time-reversed eigenstates (Figure 4.6). Note that Kramers degeneracy has been used in the proof for equal transition intensities in equation (4.79) in the assumption of the half-integer spin radical. Actually,

the degeneracy induced by the symmetry of hyperfine tensors can still lead to equation (4.79), even if the radical is integer spin. Consider two hyperfine-induced degenerate eigenstates $|u\rangle$ and $|v\rangle$ for an integer-spin radical. One can always find a pair of orthogonal eigenstates, $|\phi\rangle$ and $|\varphi\rangle$, in such degenerate subspace that satisfy $\hat{\Theta}|\phi\rangle = |\varphi\rangle$, e.g.,

$$|\phi\rangle = \frac{1}{\sqrt{2}}(|u\rangle + \hat{\Theta}|v\rangle), \quad |\varphi\rangle = \frac{1}{\sqrt{2}}(\hat{\Theta}|u\rangle + |v\rangle), \quad (4.83)$$

where equation $\hat{\Theta}^2 = \hat{\mathbb{1}}$ for integer-spin system has been used. Hence, the radiofrequency polarization would not matter in the experiments aimed at the potential avian orientation in an RF field.

4.4 Anisotropic RF field effect

A theoretical basis of the potential resonance effect of an RF field on the radical-pair spin dynamics in the absence of a static field has been provided. Unlike a weak static magnetic field that influences the singlet-triplet interconversion through modulating the (nearly) degenerate subspaces of the spin Hamiltonian (Chapter 3), a resonant RF field benefits the triplet fraction of the radical-pair spin state by inducing transitions between different degenerate subspaces. Orientation of a bird in an RF field in the absence of the static field requires that the radical-pair spin dynamics is affected anisotropically so that the reaction yield varies with respect to the direction of the RF field. This proposal is reasonable, since anisotropic hyperfine interactions are common in organic radicals.

Cryptochrome proteins in birds' retinas are so far the most likely candidate bearing magnetic sensitive radical pairs. The FAD-based radical pairs formed in cryptochromes are supposed to be a good magnetoreceptor because of the two nitrogens (i.e. N5 and N10) in the FAD radicals with nearly axial hyperfine

interactions [102]. The degeneracy, given by N5 and N10 and the hydrogens with isotropic hyperfine interactions in the FAD radical, makes it promising for the resonance to affect the radical pair spin dynamics. Spin dynamics simulations are performed for FAD-based radical pairs under an RF field so that the possibility of an RF field compass for avian magnetoreception can be evaluated. Note that the RF field in the calculation is a monochromatic field which is the sum of two counter-rotating, circularly polarized fields, i.e. a linearly polarized field. As is discussed in Section 4.3, a CP+ or CP− RF field produces equivalent resonance effect for a radical pair without the static field, so that the choice of a monochromatic field would show no favour to the CP+ or CP− component in terms of resonance effects.

4.4.1 FAD-Z radical pair

The FAD-Z radical pair, where the FAD radical is partnered by a radical ($Z^\bullet$) with no or few, weak hyperfine interactions, is normally acknowledged to be a chemical compass functioning better in sensing the weak (geomagnetic) field than the FAD-Trp radical pair [102]. Although the identity of the $Z^\bullet$ radical is still a mystery, several candidates are reasonable under certain chemical conditions (Chapter 3). Furthermore, the disruption of birds' orientation under RF fields at the geomagnetic Larmor frequency (~ 1.4 MHz) implies the existence of such a radical. N5 and N10 are included in the $FAD^{\bullet-}$ radical (Appendix A). The Hamiltonian of the time-dependent Zeeman interaction of the electron with the monochromatic RF field is

$$\hat{H}_{1(t)} = -\gamma_e B_1 \cos(\omega_{\text{rf}} t + \gamma) (\hat{S}_x \cos(\phi) \sin(\theta) + \hat{S}_y \sin(\phi) \sin(\theta) + \hat{S}_z \cos(\theta)), \quad (4.84)$$

where γ is the initial phase of the RF field which will be averaged in γ -COMPUTE, $\hat{S}_\alpha = \hat{S}_{1\alpha} + \hat{S}_{2\alpha}$ for $\alpha = x, y, z$, and $\omega_{\text{rf}}, B_1, \theta, \phi$ are those defined in Section

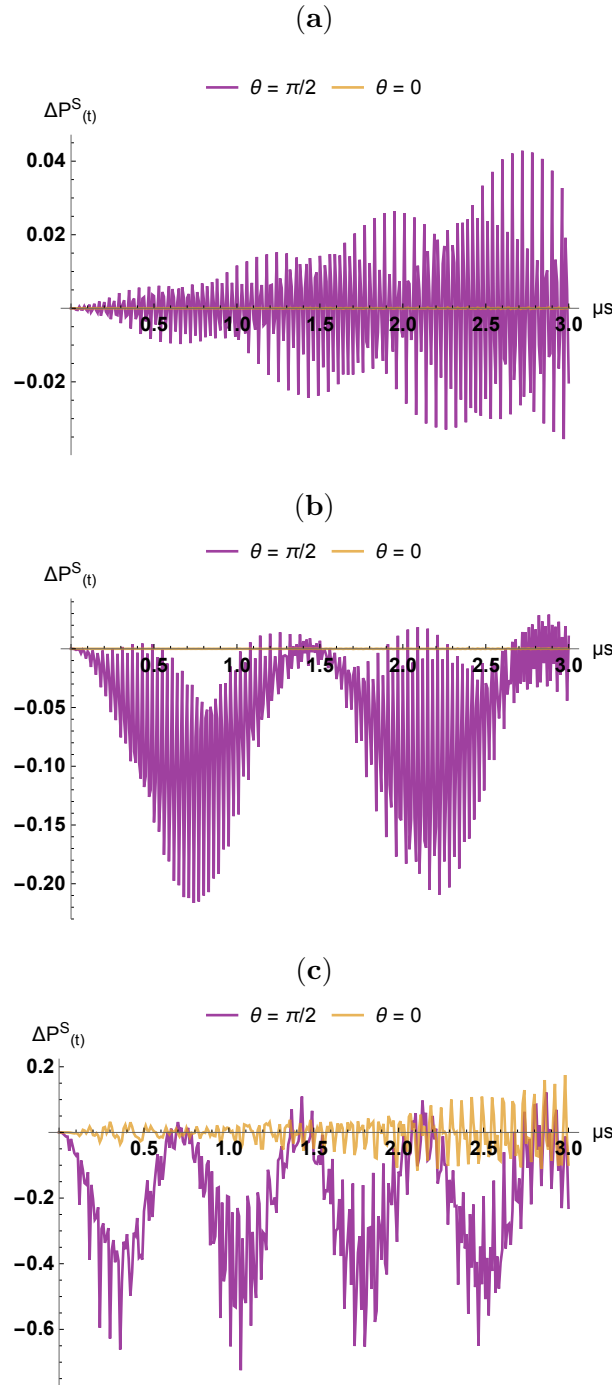


Figure 4.7: The change (calculate using γ -COMPUTE) in singlet probability ($\Delta P_{(t)}^S$), caused by the applied field in two directions ($\theta = 0$ or $\pi/2$), for the simplified FAD-Z radical pair with N5 and N10 included in the $\text{FAD}^{\bullet-}$ radical. The applied field: a $50 \mu\text{T}$ monochromatic RF field at (a) 80.0 MHz and (b) 66.3 MHz ; a $50 \mu\text{T}$ static magnetic field in (c). The discretization step n in γ -COMPUTE is chosen to be 2^7 .

4.2.2. The change in time-dependent singlet probability, $\Delta P_{(t)}^S$, brought by the RF field alone, is calculated,

$$\Delta P_{(t)}^S = P_{(B_1, \omega_{\text{rf}}, t)}^S - P_{0(t)}^S. \quad (4.85)$$

Note that in the calculation $B_1 = 50 \mu\text{T}$, comparable to the geomagnetic field. Shown in Figure 4.7(a), under an RF field at a generic off-resonant frequency, 80 MHz, the rapidly oscillating $\Delta P_{(t)}^S$ will be averaged out in the calculation of the singlet yield no matter how the RF field is oriented. In Figure 4.7(b), the RF field is at a resonant frequency, 66.3 MHz. When the RF field is oriented to the x -axis ($\theta = \pi/2$), $\Delta P_{(t)}^S$ clearly reflects the periodic transitions between eigenstates in resonance with the RF field, which gives a negative net change in the singlet fraction. Note that the superimposed rapid oscillation is attributed to the RF field effect on the coherences (equation (4.39)) and the integral by time to obtain reaction yields averages such oscillation out. Nevertheless, the modulation of the spin dynamics disappears when orienting the RF field to the z -axis ($\theta = 0$). Such anisotropic modulation of $\Delta P_{(t)}^S$ makes it promising for a chemical compass to solely rely on the direction of a resonant RF field. For comparison, $\Delta P_{(t)}^S$ under a 50 μT static magnetic field is shown in Figure 4.7(c). Clearly, both a weak static field and a resonant RF field can produce the periodic negative $\Delta P_{(t)}^S$ though with different mechanisms: the weak static field reconstructs the degenerate subspaces, whereas the RF field induces the resonance between the degenerate subspaces.

Calculation of the singlet yield under an RF field as a function of frequency makes the resonance effect clearer. Consider the symmetric reaction model where the singlet and triplet fractions react separately with the same rate constant $k = 10^6 \text{ s}^{-1}$. Applying a 50 μT monochromatic RF field along the x -axis, the singlet yield, Φ_S , shows appreciable drops at the vicinity of four specific frequencies (16.6, 32.7, 49.4 and 66.3 MHz), and Φ_S is not notably affected by the

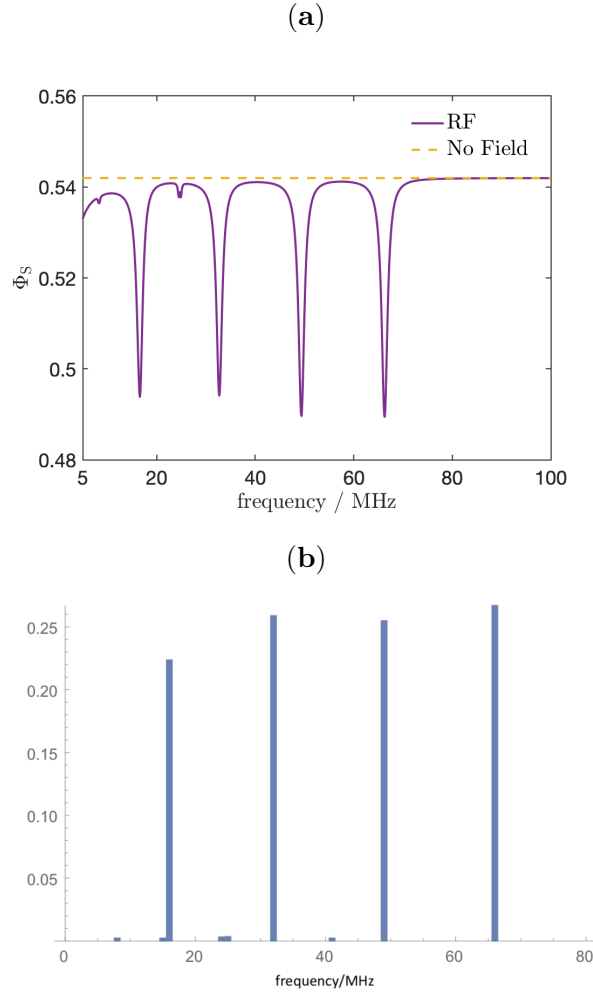


Figure 4.8: (a) Singlet yield (calculated using γ -COMPUTE) for the simplified FAD-Z radical pair, under a $50 \mu\text{T}$ monochromatic RF field along the x -axis, as a function of frequency (purple solid trace) in comparison with the zero-field radical pair (orange dashed trace). (b) Action spectrum histograms for the simplified FAD-Z radical pair.

RF field at other generic frequencies (Figure 4.8(a)). In Figure 4.8(b), “action spectrum histogram”, as a complement of the spin dynamics simulation, is shown to compare the effects of an RF field at different resonant frequencies. Action spectrum histograms in the sense of Fermi’s golden rule were previously used to characterize the disruption of the anisotropic static-field effect by RF fields [109]. Here, action spectrum histograms are calculated based on the second-order Liouville–von Neumann equation so that degeneracy is conveniently taken into account. In the interaction picture, the dynamical equation for the density matrix

$\tilde{\rho}_{(t)}$ is written,

$$\frac{d\tilde{\rho}_{(t)}}{dt} = -i[\hat{H}_{(t)}, \tilde{\rho}_{(t)}], \quad (4.86)$$

where $\hat{H}_{(t)}$ denotes the time-dependent Zeeman interaction with the RF field. To second order in time, $\tilde{\rho}_{(t)}$ is obtained as

$$\begin{aligned} \tilde{\rho}_{(t)} &\approx \left(\hat{1} - i\hat{H}_{(t)}t - \frac{1}{2}\hat{H}_{(t)}^2t^2\right)\tilde{\rho}_{(0)}\left(\hat{1} + i\hat{H}_{(t)}t - \frac{1}{2}\hat{H}_{(t)}^2t^2\right) \\ &= \tilde{\rho}_{(0)} - i[\hat{H}_{(t)}, \tilde{\rho}_{(0)}]t - \frac{1}{2}[\hat{H}_{(t)}, [\hat{H}_{(t)}, \tilde{\rho}_{(0)}]]t^2, \end{aligned} \quad (4.87)$$

where $\tilde{\rho}_{(0)} = \rho_{(0)} = \hat{P}^S/Z$. Write $\hat{H}_{(t)}$ in the eigenbasis of $\hat{H}_0$,

$$\begin{aligned} \hat{H}_{(t)} &= \mathcal{U}_{(\hat{H}_0, t)}^\dagger \hat{H}_{(t)} \mathcal{U}_{(\hat{H}_0, t)} \\ &= \sum_{p, q} |p\rangle\langle p| \hat{h} f_{(\omega_{\text{rf}}, t)} |q\rangle\langle q| e^{i(\omega_p - \omega_q)t}, \end{aligned} \quad (4.88)$$

where $\mathcal{U}_{(\hat{H}_0, t)} = e^{-i\hat{H}_0 t}$, $\hat{H}_{(t)} = \hat{h} f_{(\omega_{\text{rf}}, t)}$ in which $\hat{h}$ is the time-independent term and $f_{(\omega_{\text{rf}}, t)}$ characterizes the oscillation of the RF field. The resonance condition requires $f_{(\omega_{\text{rf}}, t)}$ to cancel the zero-quantum oscillation $e^{i(\omega_p - \omega_q)t}$. Ignoring the off-resonance elements gives:

$$\hat{H}_{(t)} \approx \hat{H}' = \sum_{\{i\}, \{j\}} (|i\rangle\langle i| \hat{h} |j\rangle\langle j| + |j\rangle\langle j| \hat{h} |i\rangle\langle i|), \quad (4.89)$$

where the RF field is assumed to induce the resonance between the degenerate subspaces (i.e. $\{i\}$ and $\{j\}$ denote the aggregates of states in the two degenerate subspaces). The change in the singlet probability brought about by the resonant RF field is

$$\begin{aligned} \Delta P_{(t)}^S &= \text{Tr}\{\mathcal{U}_{(\hat{H}_0, t)} \hat{P}^S \mathcal{U}_{(\hat{H}_0, t)}^\dagger \tilde{\rho}_{(t)}\} - \frac{1}{Z} \text{Tr}\{\mathcal{U}_{(\hat{H}_0, t)} \hat{P}^S \mathcal{U}_{(\hat{H}_0, t)}^\dagger \hat{P}^S\} \\ &\approx \frac{1}{Z} \text{Tr}\{-i\hat{P}^S [\hat{H}', \hat{P}^S]t - \frac{1}{2}\hat{P}^S [\hat{H}', [\hat{H}', \hat{P}^S]]t^2\}, \end{aligned} \quad (4.90)$$

where

$$\hat{P}^S = \sum_{\{i\}, \{j\}} (|i\rangle\langle i| \hat{P}^S |i\rangle\langle i| + |j\rangle\langle j| \hat{P}^S |j\rangle\langle j|), \quad (4.91)$$

in which the diagonal (population) elements are preserved to bear the transitions, whereas the off-diagonal (coherence) elements are ignored, for the resonance effect on them will be averaged out when calculating the singlet yield. Note that

$$\begin{aligned}
\mathbf{Tr}\{\hat{P}'^S[\hat{H}', \hat{P}'^S]\} &= \mathbf{Tr}\{\hat{P}'^S \hat{H}' \hat{P}'^S\} - \mathbf{Tr}\{\hat{P}'^S \hat{P}'^S \hat{H}'\} = 0, \\
\mathbf{Tr}\{\hat{P}'^S[\hat{H}', [\hat{H}', \hat{P}'^S]]\} &= \mathbf{Tr}\{\hat{P}'^S \hat{H}' \hat{H}' \hat{P}'^S - \hat{P}'^S \hat{H}' \hat{P}'^S \hat{H}' \\
&\quad - \hat{P}'^S \hat{H}' \hat{P}'^S \hat{H}' + \hat{P}'^S \hat{P}'^S \hat{H}' \hat{H}'\} \\
&= 2\mathbf{Tr}\{\hat{P}'^S \hat{H}' \hat{H}' \hat{P}'^S - \hat{P}'^S \hat{H}' \hat{P}'^S \hat{H}'\},
\end{aligned} \tag{4.92}$$

so that

$$\Delta P_{(t)}^S \approx -\frac{1}{Z} \mathbf{Tr}\{\hat{P}'^S \hat{H}' \hat{H}' \hat{P}'^S - \hat{P}'^S \hat{H}' \hat{P}'^S \hat{H}'\} t^2. \tag{4.93}$$

Then, the resonance effect is quantified by $\mathcal{R}$,

$$\mathcal{R} = \mathbf{Tr}\{\hat{P}'^S \hat{H}' \hat{H}' \hat{P}'^S - \hat{P}'^S \hat{H}' \hat{P}'^S \hat{H}'\}. \tag{4.94}$$

The height of each action spectrum histogram bar is $\mathcal{R}$ normalized by the sum of $\mathcal{R}$ over all energy gaps in both radicals. The drop (Figure 4.8(a)) in the singlet yield satisfactorily matches action spectrum histograms (Figure 4.8(b)) under the RF field at frequencies corresponding to energy gaps. This indicates that at frequency much higher than the reaction rate constant (~ 1 MHz), the RF field must rely on the resonance effect to cause appreciable modulation of the reaction yield. The anisotropic RF field effect is quantified by the maximum difference in singlet yield, $\Delta\Phi_S$,

$$\Delta\Phi_S = \max\{\Phi_{S(\theta, \phi)}\} - \min\{\Phi_{S(\theta, \phi)}\}. \tag{4.95}$$

Considering the axial symmetry of the hyperfine interactions of N5 and N10, only $\Phi_{S(0,0)}$ and $\Phi_{S(90^\circ, 0)}$ are calculated for each frequency. Then, the difference in the singlet yield is obtained as,

$$\Delta\Phi_S^{z-x} = \Phi_{S(0,0)} - \Phi_{S(90^\circ, 0)}. \tag{4.96}$$

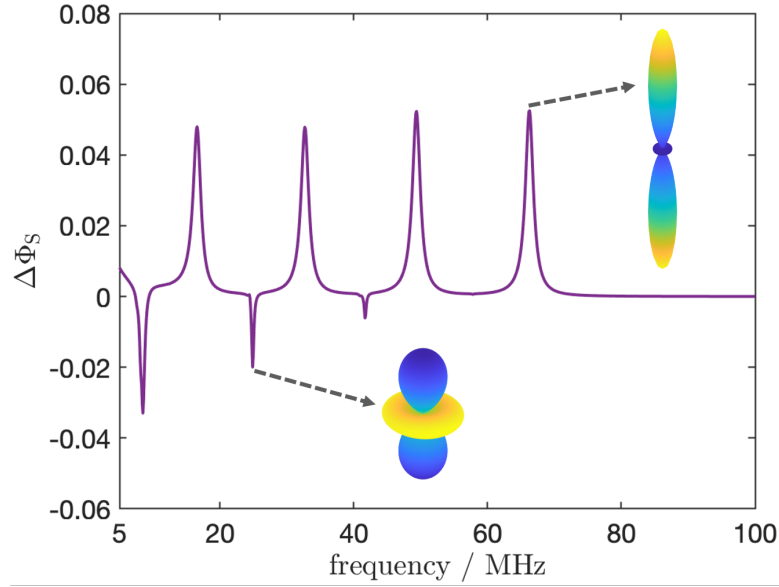


Figure 4.9: $\Delta\Phi_S = \Phi_{S(0,0)} - \Phi_{S(90^\circ,0)}$ as a function of frequency of a $50 \mu\text{T}$ monochromatic RF field for the simplified FAD-Z radical pair. Four positive ($\Delta\Phi_S > 0$) resonance (at 16.6, 32.7, 49.4 and 66.3 MHz) peaks arise from transitions between energy levels that are approximately split by the z -components of the (nearly) axial hyperfine interactions of the electron with the two nitrogens (N5 and N10 in the $\text{FAD}^{\bullet-}$ radical). Three negative ($\Delta\Phi_S < 0$) resonance (at 8.5, 24.9 and 41.7 MHz) peaks arise from transitions between energy levels that are approximately split by the x and y -components of the (nearly) axial hyperfine interactions of the electron with the two nitrogens (N5 and N10 in the $\text{FAD}^{\bullet-}$ radical). 3D polar plots (the dumbbells) for the singlet yield at 24.9 and 66.3 MHz are also illustrated.

In Figure 4.9, $\Delta\Phi_S^{z-x}$ is illustrated as a function of the frequency of the $50 \mu\text{T}$ monochromatic RF field. Except for the four frequencies that give $\Delta\Phi_S^{z-x} > 0$, there are other resonant frequencies that give $\Delta\Phi_S^{z-x} < 0$. Such reversed anisotropy pattern of the singlet yield is more clearly seen by comparing the 3D polar plots³ for singlet yield at 24.9 MHz and 66.3 MHz, shown in Figure 4.9 (note that the blue region denotes $r = \Phi_{S(\theta,\phi)} - \bar{\Phi}_S < 0$, and the yellow region denotes $r = \Phi_{S(\theta,\phi)} - \bar{\Phi}_S > 0$). This suggests that if birds orient their heads to the direction of an RF field at 66.3 MHz, they would re-orient their heads perpendicularly

³Three-dimensional angular dependence of the singlet yield for the applied field. The surface position is dictated by the polar coordinates: θ , ϕ and $|r| = |\Phi_{S(\theta,\phi)} - \langle\Phi_S\rangle|$ where $\langle\Phi_S\rangle = \frac{1}{4\pi} \iint \sin(\theta) \Phi_{S(\theta,\phi)} d\theta d\phi$ is the averaged singlet yield over all directions of the RF field.

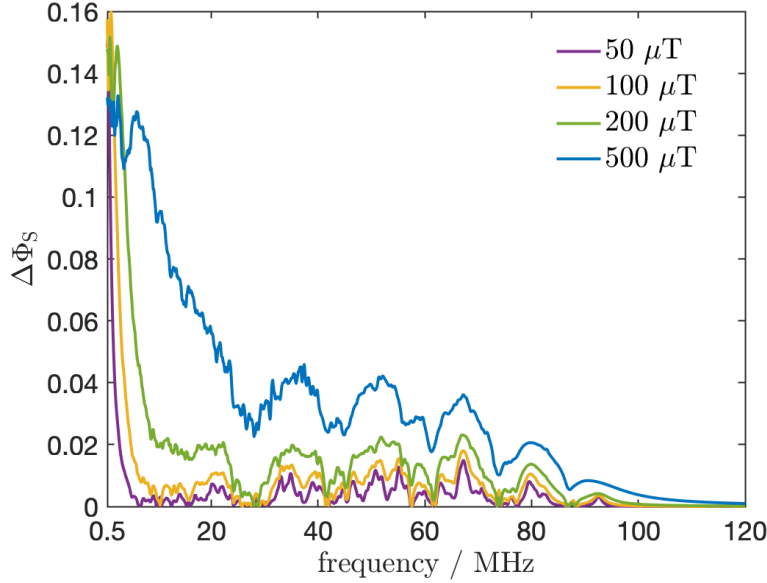


Figure 4.10: Anisotropy of the singlet yield (calculated using γ -COMPUTE), $\Delta\Phi_S$, for the semi-realistic FAD-Z radical pair with N5, N10, H6 and $3\times$ H8 are included in the $\text{FAD}^{\bullet-}$ radical, as a function of the RF frequency ranging in 0.5-120 MHz for four strengths 50, 100, 200 and 500 μT . The resonance-induced anisotropy of the singlet yield ($\Delta\Phi_S$) spreads in the frequency range $\lesssim 100$ MHz, which originates from the transitions among the energy levels of the hyperfine interactions in the $\text{FAD}^{\bullet-}$ radical.

to an RF field in the same direction but at 24.9 MHz.

More stringent evaluation of the proposed RF field compass requires the addition of other nuclei in the flavin radical. Aside from N5 and N10 with the nearly axial anisotropic hyperfine interactions, the less anisotropic H6 and the three isotropic H8 are included in the $\text{FAD}^{\bullet-}$ radical. The RF frequency ranges in 0.5-120 MHz, which covers the frequency region that has been shown to cause disorientation in the presence of the geomagnetic field (i.e. the resonant RF fields). In Ref [102], under a 50 μT static field, $\Delta\Phi_S$ falls from 0.206 to 0.160 when the four hydrogens are added, so that the hydrogens do not reduce the anisotropy too much. However, under a 50 μT RF field, $\Delta\Phi_S$ drops from ~ 0.05 (Figure 4.9) to ~ 0.01 (Figure 4.10) at the vast resonance region (5-100 MHz) by adding the hydrogens to the two nitrogens. This is because the number of energy levels

grows as more hydrogens are put into the system, which directly weakens the resonance effect for a single energy gap (see equation (4.41) for the increasing Z). The loss of the directional sensitivity of a resonant RF field, as a result of the addition of hydrogens, can be recouped by increasing B_1 . $\Delta\Phi_S$ reaches 0.04 under a $500\ \mu\text{T}^4$ RF field at 50 MHz. This is attributed to the increase of the width of each resonant frequency when the strength of the RF field is increased. Thus, the effect on $\Delta\Phi_S$ of a single-frequency RF field is the composition of effects of all the neighbored resonant frequencies. Note that the six largest hyperfine interactions have been included and the addition of the other nuclear spins with small hyperfine interactions in the FAD radical mainly gives rise to denser resonant frequencies distributed in the range $\lesssim 100$ MHz. Therefore, the risk of further decreasing the resonance induced $\Delta\Phi_S$ is low. Furthermore, $\Delta\Phi_S$ induced by the RF field at low frequencies is comparable to $\Delta\Phi_S = 0.16$ by the $50\ \mu\text{T}$ static weak magnetic field (e.g. In Figure 4.10, for a $100\ \mu\text{T}$ monochromatic RF field at 1 MHz, $\Delta\Phi_S = 0.150$). This means that at such low frequencies, the RF field does not rely on the resonance effect to produce an appreciable $\Delta\Phi_S$, but anisotropically modulates the radical pair spin dynamics in analogy with the static field. Note that a magnetite crystal large enough to align in the Earth's field would be too big to re-orient a million times per second. Hence, the proposed orientation of birds under low frequency ~ 1 MHz RF fields can still be a strong evidence for the radical-pair based magnetoreception.

4.4.2 FAD-Trp radical pair

The existence of a biologically reasonable FAD-Z radical pair coincides with the proposal in Ref [46], though a feasible $Z^\bullet$ radical still has not been discovered in cryptochromes. Recent study [79] suggests that the FAD-Trp radical pair,

⁴Although at the moment the RF field of several hundred microtesla is not quite feasible in practice, in principle these very difficult experiments can potentially be done.

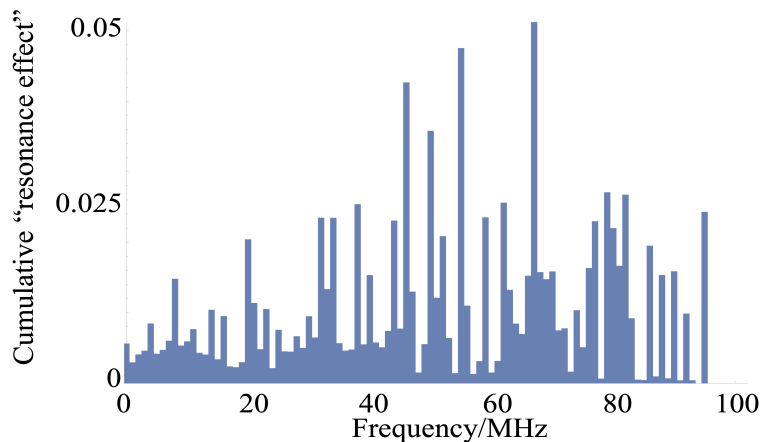


Figure 4.11: Action spectrum histograms for the semi-realistic FAD-TrpH radical pair. Cumulative “resonance effect” is the normalized $\mathcal{R}$ defined in equation (4.94).

formed by sequential electron transfers from the tryptophan tetrad to the photo-excited flavin, is probably responsible for sensing the magnetic field. A realistic FAD-Trp radical pair is too large to be accessible by γ -COMPUTE. Instead, the action spectrum histograms are still available as an approximate evaluation of the resonance effect. As is shown in Figure 4.11, the range of resonant frequencies is still below ~ 100 MHz (nuclei included in the $\text{FAD}^{\bullet-}$ radical: N5, N10, H6 and $3\times\text{H8}$, and in the $\text{TrpH}^{\bullet+}$ radical: N1, H1, H2, H4, H6, H7 and $\text{H}\beta$). Thus, we suppose that either for the FAD-Z radical pair or for the FAD-Trp radical pair, the RF field, under which birds tend to orient with respect to the field direction, is not expected to have frequency that far exceeds 100 MHz⁵.

Test of the quantum needle

The “quantum needle” hypothesis proposed by Hiscock *et al.* [56] formulates the theoretical basis for the radical-pair magnetoreceptor with high angular precision. The needle is referred to as a spike in the reaction yield when the external weak magnetic field is oriented in certain directions, for a radical pair with a

⁵Latest calculation by Wong *et al.*, including all nuclear spins in the FAD-Trp radical pair, gives 115 MHz as the maximum frequency.

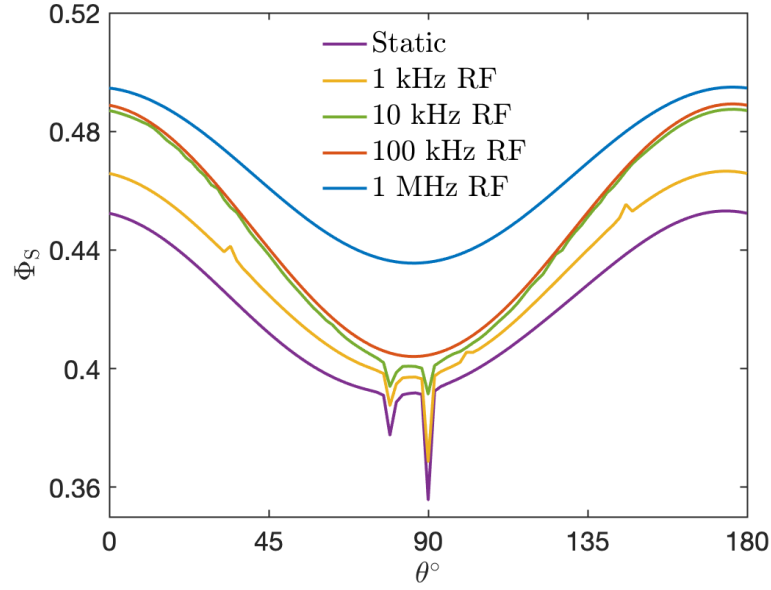


Figure 4.12: Singlet yield (calculated using γ -COMPUTE) for the simplified FAD-TrpH radical pair (lifetime $100 \mu\text{s}$) with N5 included in the $\text{FAD}^{\bullet-}$ radical and N1 included in the $\text{TrpH}^{\bullet+}$ radical as a function of the direction (θ in the range in $[0, 180^\circ]$) of the applied magnetic (static or RF) field (strength $50 \mu\text{T}$). The discretization step n in γ -COMPUTE is chosen to be 2^{11} .

lifetime longer than $1 \mu\text{s}$. The spike, arising from avoided crossings of the quantum mechanical spin energy levels of radicals, requires both radicals to contain anisotropic hyperfine interactions, which is satisfied by the FAD-Trp radical pair in cryptochromes. However, direct detection of the needle is challenging, though conditions, such as the relaxation time and the inter-radical interactions, for the existence of the spike could possibly be evaluated in cryptochromes.

The RF field at low frequency could serve as a discriminator on whether avian magnetoreception inevitably relies on the quantum needle. Calculation was performed for a simplified FAD-Trp radical pair where N5 in the $\text{FAD}^{\bullet-}$ radical and N1 in the $\text{TrpH}^{\bullet+}$ radical are included. In Figure 4.12, two spikes in the singlet yield is clearly seen for the radical pair with a lifetime $\sim 100 \mu\text{s}$ under a $50 \mu\text{T}$ static magnetic field. Replacing the static field by a 1 kHz monochromatic

RF field ($B_1 = 50 \mu\text{T}$) preserves the spike. Nevertheless, the RF field at >100 kHz removes the spike, though it can still produce a comparable anisotropy of the singlet yield. Thus, the test protocol for the quantum needle is:

1. Orientation of birds happens either under a weak static field or under an RF field with comparable strength at frequency throughout 1 kHz to 1 MHz. Possibilities accounting for birds' orientation are:
 - (a) FAD-Trp radical pairs participate in sensing the weak magnetic field, either static or radiofrequency. However, the needle does not play a significant role in the magnetoreception, as no spike of the singlet yield is expected to emerge under an RF field at frequency > 100 kHz;
 - (b) The magnetic sensing process potentially relies on the FAD-Z radical pairs where the partner radical $Z^\bullet$ does not contain an appreciable anisotropic hyperfine interaction and no spike can emerge [56]. The needle is thus not significant in avian magnetoreception;
 - (c) The lifetime of the radical pair in cryptochromes is not long enough for the production of the needle. The anisotropy of the reaction yield without the spike could sufficiently serve as the navigation information for birds to orient.
2. Birds could orient either under the weak static field or under an RF field at frequency ~ 1 kHz, but they lose the ability to orient under an RF field at frequency > 100 kHz. Then, two possibilities are presented:
 - (a) The frequency at the order of 1 kHz is too slow relative to the reaction rate constant, so that an RF field at such frequency is functioning as a static field. However, birds are intrinsically prevented from using an RF field, with a fluctuation period much shorter than the radical-pair

lifetime, to orient by some unknown effect. Then, the role of the needle is still in mystery;

- (b) Birds indeed have the ability to orient by an RF field compass. The frequency ~ 1 MHz destroys the needle, which is the critical identity for sensing the direction of the external magnetic field, so that birds are unable to show any orientation.

- 3. Birds are able to orient under a weak static field, but they could not orient under an RF field at any frequency even as low as 1 kHz. This implies that the avian magnetic compass is restricted to the orientation by a static magnetic field. Then, the role of the enhancement of the angular precision by the potential quantum needle in the avian magnetoreception would still be unclear.

4.5 Conclusion

The disruption of birds' ability to orient under a weak ($\sim 50 \mu\text{T}$) static magnetic field by RF fields ~ 10 nT has been reported by previous behavioural experimental studies, though it is still unclear how the effect of such extremely weak RF fields on the radical-pair spin dynamics is sensed by birds. Such experiments cannot exclude the possibility that the disorientation arises from some effects other than interference with the primary magnetoreception events. Orientation of birds under an RF field in the absence of the static fields, rather than disorientation under a static field by RF fields, would provide clear evidence for the direct involvement of radical pairs in the compass magnetoreceptor.

Theoretical analysis clearly shows that the resonance induced by an RF field could promote the efficiency of the singlet-triplet interconversion of a singlet born radical pair so that the triplet fraction would benefit. The modulation

of the reaction yield by a resonant RF field relies on the transitions between eigenstates in the initial radical pair spin state, rather than the resonance effect on coherences which would be averaged out during the radical-pair recombination. As a result of time-reversal symmetry of the zero-field radical pair, the resonance effect on the reaction yield requires the (near) degeneracy of spin interactions, which is sufficient in a FAD-based radical pair. Moreover, the resonance between degenerate subspaces would not select the radiofrequency polarization for the zero-field radical pair, so that in the proposed experiment of RF induced avian orientation, the polarization of the RF field is restricted. Calculation on the FAD-Z radical pair shows that the resonance-induced modulation of the reaction yield is anisotropic with respect to the direction of the RF field, though such effect could be reduced by taking into account the hydrogen spins with less anisotropic hyperfine interactions. Increasing the strength of the RF field (to $\sim 500 \mu\text{T}$) could improve the anisotropy of reaction yields to a notable extent. Furthermore, the resonance effect is not expected to emerge beyond $\sim 100 \text{ MHz}$ for both the FAD-Z and FAD-TrpH radical pairs. A monochromatic RF field at low frequency $\sim 1 \text{ MHz}$ could cause comparable anisotropy of the reaction yield with that from the geomagnetic (static) field, though the “quantum needle” would not show up. Thus, if birds could orient under an RF field at such low frequency, the role of the needle in avian magnetoreception would then be suspected.

Chapter 5

Singlet-triplet dephasing leads to time-dependent magnetic field effects and its effect on magnetoreception of weak fields

Weak magnetic fields can affect the product yields of radical pair reactions by altering the interconversion of the singlet and triplet electronic states of the two radicals [97]. The time required for this, as discussed in Chapter 2, is of the order of the electron Larmor period, $(-\gamma_e B/2\pi)^{-1}$, which is ~ 700 ns for the Earth's magnetic field ~ 50 μ T. Therefore, to be a geomagnetic sensor, the radical pair must persist for ~ 700 ns and so must the spin coherence [97]. It is easier to imagine how the former could be achieved in practice. Processes that limit the lifetime of a radical pair in cryptochrome include electron transfer between the radicals and changes in their protonation states [97], which depend on factors such as redox potentials, separations between radicals, and availability of proton donors/acceptors, all of which could have been tuned by evolution.

Spin relaxation is potentially more of a problem. It arises from stochastic molecular motions which cause fluctuations in the local magnetic fields experienced by the electrons [63–65]. The effect is to destroy spin coherence and more generally

to equilibrate the electron spins with their immediate surroundings. With the exception of small organic radicals undergoing rapid (picosecond) rotational diffusion in non-viscous liquids, electron spin relaxation as slow as ~ 700 ns is uncommon and it is unclear how this could be achieved for radicals inside a protein in a cellular setting at physiological temperatures ($\sim 40^\circ$). Relatively little is known about the rates and mechanisms of spin relaxation of FAD and tryptophan radical pairs in cryptochromes. All-atom molecular dynamics simulations of a plant cryptochrome, combined with Redfield theory, suggest relaxation times of the order of 100 ns [63] while behavioural experiments on Eurasian blackcaps imply somewhat slower spin equilibration (2-10 μ s) *in vivo* [122].

Direct measurements of spin relaxation in radical pairs are difficult and little progress has been made to date. EPR (electron paramagnetic resonance) spectroscopy in a magnetic field of ~ 50 μ T is technically challenging, especially when the radicals are short-lived and, ideally, in an environment that resembles the largely unknown conditions *in vivo*. An indirect source of information on the spin relaxation of radical pairs in cryptochromes exploits the effect of much stronger magnetic fields on their reactivity. Typically, for magnetic fields up to about 100 mT, the quantum yields of the products of radical pair reactions have a sigmoidal dependence on the intensity of the applied magnetic field characterised by a parameter, $B_{1/2}$, which is the field at which the reaction yield equals the mean of the yields at zero field and at high field:

$$\Phi_{(B_{1/2})} = \frac{\Phi_{(0)} + \Phi_{(\infty)}}{2}. \quad (5.1)$$

The measured value of $B_{1/2}$ for a particular radical pair contains information on the hyperfine interactions in the radicals, on the lifetime of the pair and on spin relaxation [53, 123]. According to the Weller equation [123], the value of $B_{1/2}$ is

assumed to be determined solely by the isotropic interactions:

$$B_{1/2} = 2\sqrt{3} \left(\frac{\sigma_{\text{FAD}}^2 + \sigma_{\text{Trp}}^2}{\sigma_{\text{FAD}} + \sigma_{\text{Trp}}} \right), \quad (5.2)$$

where σ_{FAD} and σ_{Trp} are the effective isotropic hyperfine interactions in the two radicals, defined as

$$\sigma_J = \sqrt{\frac{1}{3} \sum_i a_{Ji}^2 I_{Ji} (I_{Ji} + 1)} \quad (5.3)$$

where a_{Ji} and I_{Ji} are, respectively, the isotropic hyperfine interaction constant and the spin quantum number (1/2 for ^1H , 1 for ^{14}N) of nuclear spin i in radical J . Using hyperfine data for $\text{FAD}^{\bullet-}$ and $\text{TrpH}^{\bullet+}$ in Ref [53], we obtain: $\sigma_{\text{FAD}^{\bullet-}} = 0.70$ mT and $\sigma_{\text{TrpH}^{\bullet+}} = 0.97$ mT and hence, from equation (5.3), $B_{1/2} = 3.0$ mT. Clearly, no time-dependence of $B_{1/2}$ is predicted by equation (5.2), whereas it has been repeatedly measured [124, 125] by cavity ring-down spectroscopy (CRDS) experiments [126] that $B_{1/2}$ grows as a function of time characterized by the pump-probe delay t_d [53]. Moreover, all values of $B_{1/2(t_d)}$ for the cryptochrome mutants of three avian species exceed 3.0 mT, suggesting that electron spin relaxation influences the spin dynamics of the radical pair and hence its magnetic sensitivity. Then, it is significant to find the appropriate spin relaxation mechanism in Cry4a and investigate its influence on the effect of applied magnetic fields larger than the intra-radical (hyperfine) magnetic fields, known as the high field effect (HFE), since in the CRDS experiments, the applied magnetic fields are in the range $0 < B < 30$ mT.

Data of CRDS experiments

W369F mutants of Cry4a proteins (the fourth tryptophan (W369) of the Trp-tetrad (Trp_D) is replaced by a phenylalanine [79]) from the migratory European robin (*Erithacus rubecula*, *Er*), and two non-migratory birds, pigeon (*Columba livia*, *Cl*) and chicken (*Gallus gallus*, *Gg*) are studied in the CRDS experiments.

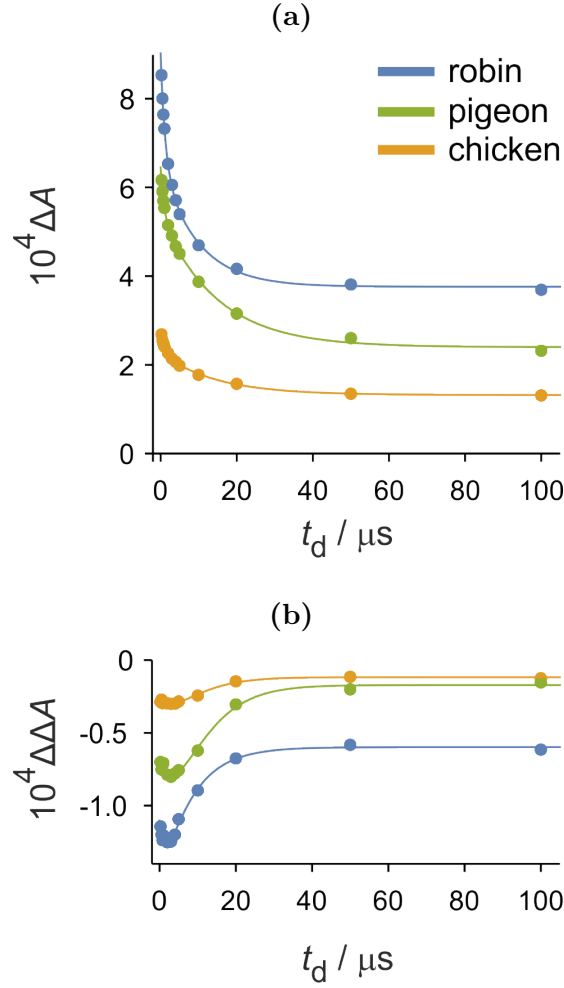


Figure 5.1: Time-dependence of the absorbance (at a probe wavelength of 530 nm) changes for the W369F mutants of robin, chicken and pigeon Cry4a. (a) $\Delta A_{(t_d, 0)}$ with fits to the biexponential model function, $A_0 + A_1 e^{-t_d/t_1} + A_2 e^{-t_d/t_2}$. The best-fit parameters are given in Table 5.1. (b) $\Delta \Delta A_{(t_d, 30\text{mT})}$, the change in absorbance produced by a 30 mT magnetic field. **Note** that the experimental and fitted data are from the D.Phil. thesis of Matthew Golesworthy [125].

Note that all the experimental and fitted data used in Figures 5.1 and 5.2 and in Tables 5.1 and 5.2 are from the D.Phil. thesis of Matthew Golesworthy [125]. The time-dependent change $\Delta A_{(t_d)}$, in the wavelength-dependent absorbance A [127, 128], as a result of photoexcitation of the proteins is recorded to characterize the reaction yields of the products and the fraction of radical pairs that remain at time t_d . The magnetic field effect is quantified by the measurement of the difference in $\Delta A_{(t_d)}$ with and without an external magnetic field:

	robin	chicken	pigeon
$t_1 / \mu\text{s}$	1.21	1.17	0.96
$t_2 / \mu\text{s}$	9.59	14.4	14.7
$10^4 A_0$	3.76	1.32	2.40
$10^4 A_1$	2.46	0.509	1.08
$10^4 A_2$	2.80	0.956	2.97
MFE	21%	14%	17%

Table 5.1: Fit parameters for the data in Figure 5.1(a) for Cry4a W369F mutants. The final row gives the peak relative magnetic field effect, defined as the maximum value of $|\Delta\Delta A_{(t_d, 30\text{mT})}/\Delta A_{(t_d, 0)}|$.

$$\Delta\Delta A_{(t_d, B)} = \Delta A_{(t_d, B)} - \Delta A_{(t_d, 0)}, \quad (5.4)$$

which is dependent on time and varies with respect to the strength of the applied magnetic field. Figure 5.1(a) shows the absorbance changes, $\Delta A_{(t_d, 0)}$, measured in the absence of an applied magnetic field, for each of the proteins as a function of the pump-probe delay. Also shown in Figure 5.1(a) are fits to a biexponential model function [125], $A_0 + A_1 e^{-t_d/t_1} + A_2 e^{-t_d/t_2}$, for $0 < t_d < 100 \mu\text{s}$. The fit parameters are shown in Table 5.1. The absolute magnetic field effects, $|\Delta\Delta A_{(t_d, 30\text{mT})}|$, are in the order robin > pigeon > chicken and the peak relative magnetic field effects, defined as the maximum value of $|\Delta\Delta A_{(t_d, 30\text{mT})}/\Delta A_{(t_d, 0)}|$, are: robin 21%, chicken 14%, and pigeon 17%.

In a separate series of experiments, the change in absorbance $\Delta\Delta A_{(t_d, B)}$, produced by magnetic fields in the range $0 < B < 30 \text{ mT}$ at five pump-probe delays ($t_d = 0.25, 0.50, 2.0, 5.0$ and $10 \mu\text{s}$) spanning the decay of the fast component ($t_1 \approx 1 \mu\text{s}$) of the kinetics in Figure 5.1(a), is measured. For each t_d , $\Delta\Delta A_{(t_d, B)}$ is illustrated as a function of the magnetic field strength B , as is shown in Figure 5.2, which is the so-called magnetically altered reaction yield (MARY) curve [53, 79]. All three proteins display the sigmoidal magnetic field-dependence

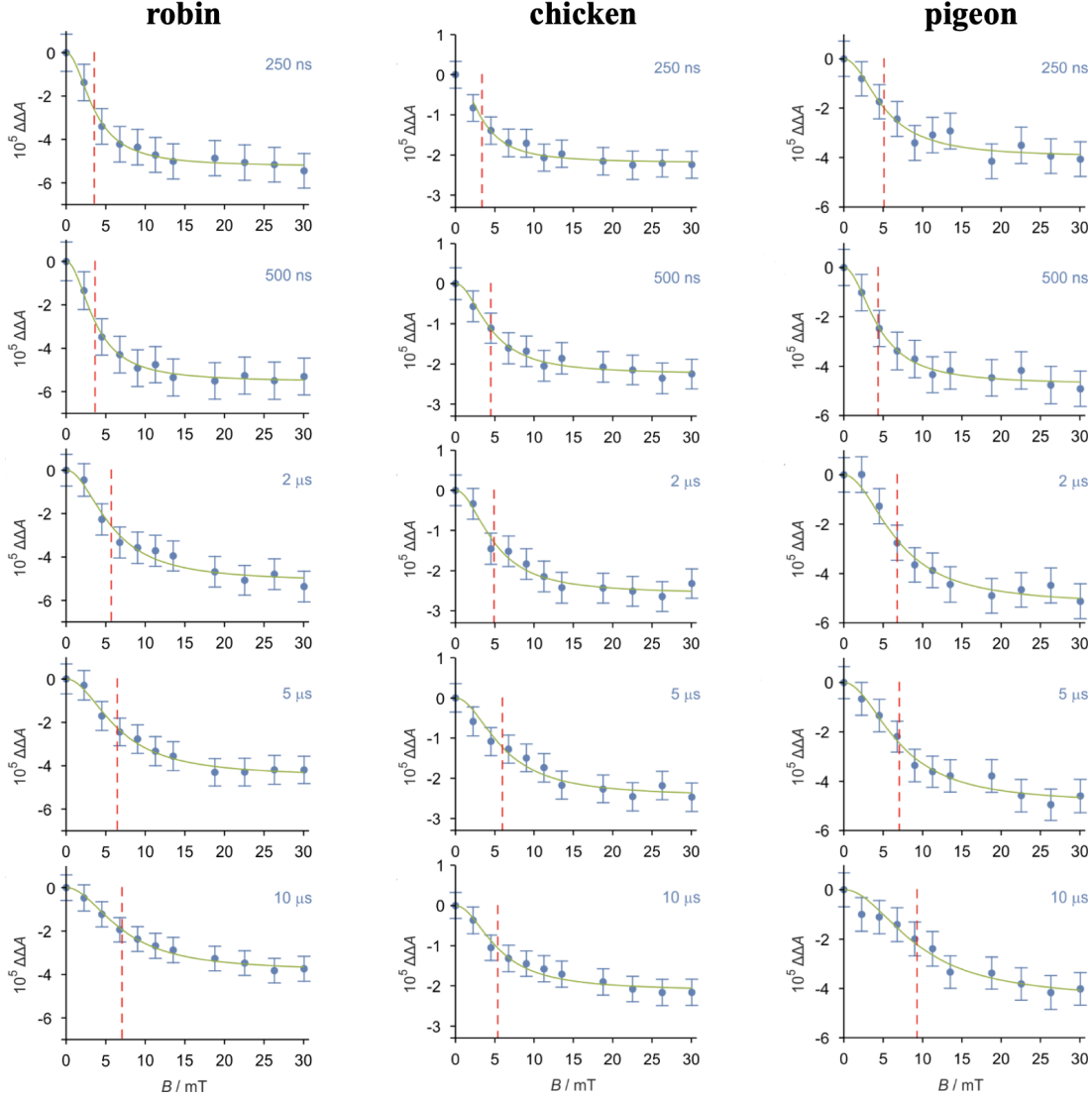


Figure 5.2: Magnetic field-dependence of the light-induced changes in the absorbance of *ErCry4a* W369F (**robin**), *GgCry4a* W369F (**chicken**) and *ClCry4a* W369F (**pigeon**) at pump-probe delays of 250 ns, 500 ns, 2 μ s, 5 μ s, 10 μ s. The green lines are fits to equation (5.6). In each panel, the error bars represent ± 1.0 standard deviation of the residuals (i.e. fit minus data). The dashed red lines mark the values of $B_{1/2}(t_d)$ obtained by fitting to equation (5.6).

characteristic of the radical pair mechanism. Then, the value of $B_{1/2}$ for each t_d in a MARY curve is the strength of the magnetic field under which the difference of the change in absorbance reaches the half of that by the strongest magnetic field applied,

$$\Delta\Delta A_{(t_d, B_{1/2})} = \frac{1}{2} \Delta\Delta A_{(t_d, 30 \text{ mT})}. \quad (5.5)$$

$t_d / \mu s$	robin	chicken	pigeon
0.25	3.55 ± 0.16	3.39 ± 0.26	5.10 ± 0.58
0.50	3.64 ± 0.17	4.50 ± 0.32	4.35 ± 0.26
2.0	5.70 ± 0.48	4.91 ± 0.44	6.75 ± 0.56
5.0	6.45 ± 0.35	5.97 ± 0.61	7.08 ± 0.53
10.0	7.05 ± 0.32	5.40 ± 0.42	9.33 ± 0.97

Table 5.2: Values of $B_{1/2}(t_d)$ (in mT) for Cry4a W369F mutants obtained from the data in Figure 5.2.

Also shown in Figure 5.2 are fits of the data to a Lorentzian model,

$$f(t_d) = h(t_d) \left(1 - \frac{1}{1 + (B/B_{1/2}(t_d))^2} \right), \quad (5.6)$$

in which $h(t_d)$ is the limiting value of $\Delta\Delta A_{(t_d, B)}$ at high field (in practice, ~ 30 mT). The values of $B_{1/2}(t_d)$ so obtained are given in Table 5.2. The trend for all three proteins is for $B_{1/2}(t_d)$ to increase with increasing pump-probe delay.

5.1 Spin dynamics modelling

The photo-excitation of the FAD co-factors in wild-type Cry4a proteins is followed by sequential electron transfer involving four tryptophans, which forms FAD-Trp radical pairs [79] that may account for avian magnetoreception. In W369F mutants, the electron transfer along the tryptophan chain produces three radical-pair states RP_X ($X = A, B$ and C). The two steps of the radical-pair formation, $RP_A \rightarrow RP_B$ and $RP_B \rightarrow RP_C$, are exergonic, rapid, and outpace the reverse reactions ($RP_A \leftarrow RP_B$ and $RP_B \leftarrow RP_C$). RP_C has a lifetime $\sim 1 \mu s$ (see Table 5.1) [79], which allows the applied magnetic field to modulate the radical-pair spin dynamics and affect the yields of reaction products. In Figure 5.3, the reaction scheme for RP_C , including the spin selective recombination and the spin-independent deprotonation of the $Trp_C H^{\bullet+}$ radical, is illustrated. Change in absorbance (highest for *Er*Cry4a and the lowest for *Gg*Cry4a in Figure 5.1(a))

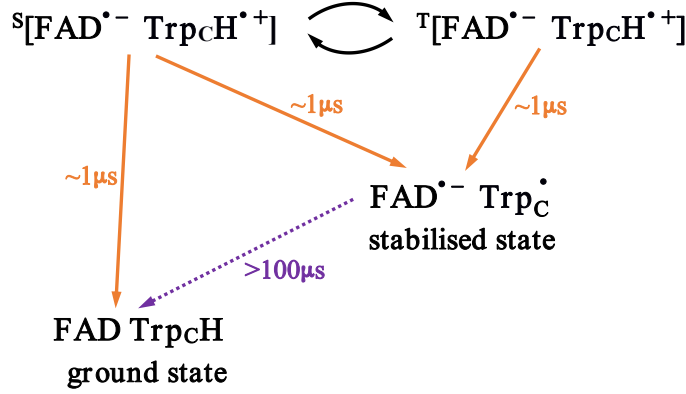


Figure 5.3: Reaction scheme for RP_C in the W369F mutant of Cry4a. The rate constants for the recombination of the $[FAD^{\bullet-} Trp_C H^{\bullet+}]$ radical pair and the deprotonation of the $Trp_C H^{\bullet+}$ radical are $\sim 1 \mu s^{-1}$. The reduction of $Trp^{\bullet}$ to $TrpH$ takes $> 20 \mu s$ (Figure 5.1(b) and Table 5.1) [125]. It takes more than $100 \mu s$ for the $FAD^{\bullet-}$ radical to return to the ground state FAD [79].

decays by $\sim 50\%$ in the first $50 \mu s$ leaving a signal with lifetime greater than $100 \mu s$, attributed to the $FAD^{\bullet-} Trp_C^{\bullet}$ state (Figure 5.3) of the proteins. According to the biexponential fit parameters shown in Table 5.1, t_1 ($\sim 1 \mu s$) is attributed to a combination of back electron transfer (with rate constant k_r) in the singlet radical pair, $^s[FAD^{\bullet-} Trp_C H^{\bullet+}]$, and deprotonation of $Trp_C H^{\bullet+}$ (with rate constant k_f) to give $FAD^{\bullet-} Trp_C^{\bullet}$. t_2 ($10\text{--}15 \mu s$) is supposed to characterize the kinetics of the reduction (with rate constant k_p) of $Trp_C^{\bullet}$ to give $Trp_C H$. This accounts for the rise of $\Delta\Delta A_{(t_d, 30 \text{ mT})}$ in the pump-delay $t_d \lesssim 20 \mu s$ (Figure 5.1(b)), given that $TrpH$ has no absorbance at 530 nm [129]. t_2 also contains the kinetics of the possible recombination (with rate constant k_b) of the singlet $FAD^{\bullet-} Trp_C^{\bullet}$. The method of including the recombination of $FAD^{\bullet-} Trp_C^{\bullet}$ in the spin dynamics simulation is demonstrated in Appendix D, though it does not need to be considered for the spin dynamics modelling in this chapter. This is because in the time scale of $> 10 \mu s$ (t_2), the spin state of $FAD^{\bullet-} Trp_C^{\bullet}$ is already relaxed, and the external magnetic field is therefore not expected to appreciably modulate the spin dynamics of $FAD^{\bullet-} Trp_C^{\bullet}$ [79, 84]. Therefore, in the spin dynamics simulation, it is appropriate to consider that the applied magnetic field solely influences the singlet-triplet

interconversion in the $[\text{FAD}^{\bullet-} \text{ Trp}_\text{C}\text{H}^{\bullet+}]$ radical pair.

5.1.1 Spin relaxation

The time-dependent MARY curves for the W369F mutants of Cry4a proteins of all three avian species have shown the profound time-dependence of $B_{1/2}$ (Figure 5.2), the source of which is anticipated to be electron spin relaxation. The three most probable spin relaxation mechanisms for the FAD-based radical pairs in Cry4a (i.e. random fields relaxation, singlet-triplet dephasing and triplet-triplet dephasing) have been included separately in the simulation of a simple radical pair, in which each radical has a nitrogen with an isotropic interaction. The hyperfine constants of the two radicals are: $a_1 = 0.523$ mT (as N5 in $\text{FAD}^{\bullet-}$) and $a_2 = 0.322$ mT (as N1 in $\text{TrpH}^{\bullet+}$). The magnetic field effect was assessed by means of the yield of the product formed from the triplet state of the radical pair, which is referred to as the “triplet yield”, $\Phi_{\text{T}(t_d, B)}$, used here in order that the magnetic field effects have the same sign as in the MARY curves in Figure 5.2, i.e. $\Phi_{\text{T}(t_d, 0)} > \Phi_{\text{T}(t_d, B)}$. The dynamical equation for the radical-pair spin state in Liouville space is:

$$\frac{d\sigma(t)}{dt} = -\hat{L}\sigma(t), \quad (5.7)$$

where $\sigma(t)$ is the the row-wise flattened (vectorised) form of the density matrix, and $\hat{L} = i\hat{H} + \hat{K} + \hat{W}$ is the Liouvillian superoperator, in which $\hat{H} = \hat{H} \otimes \hat{1} - \hat{1} \otimes \hat{H}^\text{T}$ is the Hamiltonian commutation superoperator, $\hat{K}$ is the chemical reaction superoperator, where we have adopted the symmetric reaction approximation, with reaction rate constants $k = k_\text{S} = k_\text{T} = 10^6 \text{ s}^{-1}$ so that

$$\hat{K} = \frac{k_\text{S}}{2}(\hat{P}^\text{S} \otimes \hat{1} + \hat{1} \otimes \hat{P}^\text{S}) + \frac{k_\text{T}}{2}(\hat{P}^\text{T} \otimes \hat{1} + \hat{1} \otimes \hat{P}^\text{T}) = k\hat{1}, \quad (5.8)$$

and $\hat{W}$ is the relaxation superoperator. Thus,

$$\sigma(t) = e^{-\hat{L}t}\sigma(0), \quad (5.9)$$

5.1. Spin dynamics modelling

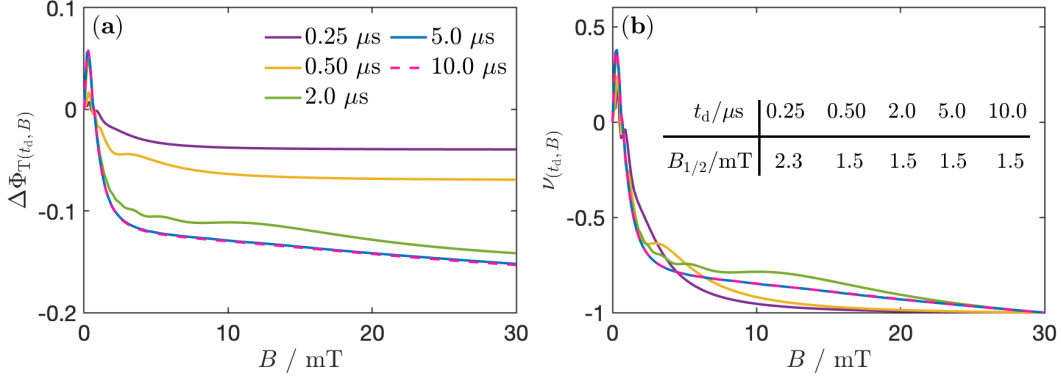


Figure 5.4: A simple radical pair (each radical includes an isotropic nitrogen with the hyperfine parameters, $a_1 = 0.523$ mT and $a_1 = 0.322$ mT) with lifetime of $1 \mu\text{s}$. (a) The change in the triplet yield, $\Delta\Phi_{T(t_d, B)}$, as a function of magnetic field strength for five pump-probe delays ($0.25, 0.50, 2.0, 5.0$ and $10.0 \mu\text{s}$). (b) $\Delta\Phi_{T(t_d, B)}$ is normalized by $|\Delta\Phi_{T(t_d, 30 \text{ mT})}|$ to obtain $\nu(t_d, B)$.

where for the singlet born radical pair $\sigma_{(0)} = (1/Z) \sigma^S$, where Z is the nuclear spin dimension and $\sigma^{S(T)}$ is the row-wise flattened (vectorised) form of $\hat{P}^{S(T)}$. Then, the time-dependent triplet yield $\Phi_{T(t_d)}$ is obtained as:

$$\Phi_{T(t_d, B)} = k \int_0^{t_d} (\hat{\sigma}^T)^\top \sigma(t) dt = \frac{k}{Z} (\hat{\sigma}^T)^\top \hat{L}^{-1} (\hat{\mathbb{1}} - e^{-\hat{L} t_d}) \hat{\sigma}^S. \quad (5.10)$$

where the superscript “ $\top$ ” denotes transpose. The time-dependent magnetic field effect is thus quantified by $\Delta\Phi_{T(t_d, B)} = \Phi_{T(t_d, B)} - \Phi_{T(t_d, 0)}$. Figure 5.4(a) shows $\Delta\Phi_{T(t_d, B)}$ as a function of B for five pump-probe delay time ($t_d = 0.25, 0.5, 2, 5$ and $10 \mu\text{s}$) without spin relaxation. Both the low field ($B < 1$ mT) and high field ($B > 1$ mT) effects can be seen: the positive $\Delta\Phi_{T(t_d, B)}$, corresponding to the low field effect, is due to the weak magnetic field effect on the (nearly) degenerate subspaces [54], whereas the negative $\Delta\Phi_{T(t_d, B)}$, corresponding to the high field effect, is the result of the energy splitting between the singlet and triplet states induced by the strong magnetic field, which greatly hinders the singlet-triplet interconversion. In order to compare the $B_{1/2}$ values at different t_d , $\Delta\Phi_{T(t_d, B)}$ is normalized by $|\Delta\Phi_{T(t_d, 30 \text{ mT})}|$:

$$\nu(t_d, B) = \frac{\Delta\Phi_{T(t_d, B)}}{|\Delta\Phi_{T(t_d, 30 \text{ mT})}|}. \quad (5.11)$$

Thus, $\nu_{(t_d, B_{1/2})} = -0.5$. Clearly in Figure 5.4(b), $B_{1/2}$ does not increase with time when no relaxation mechanism is taken into account.

Random fields relaxation

Random fields relaxation (RFR) is a generic mechanism in which the two electron spins are relaxed isotropically with equal rate constants due to the fluctuation of the local magnetic fields experienced by the two electrons [65, 130]. The field fluctuation can be attributed to the stochastic modulation of hyperfine interactions caused by fluctuations in dihedral angles and librational motions of the radicals

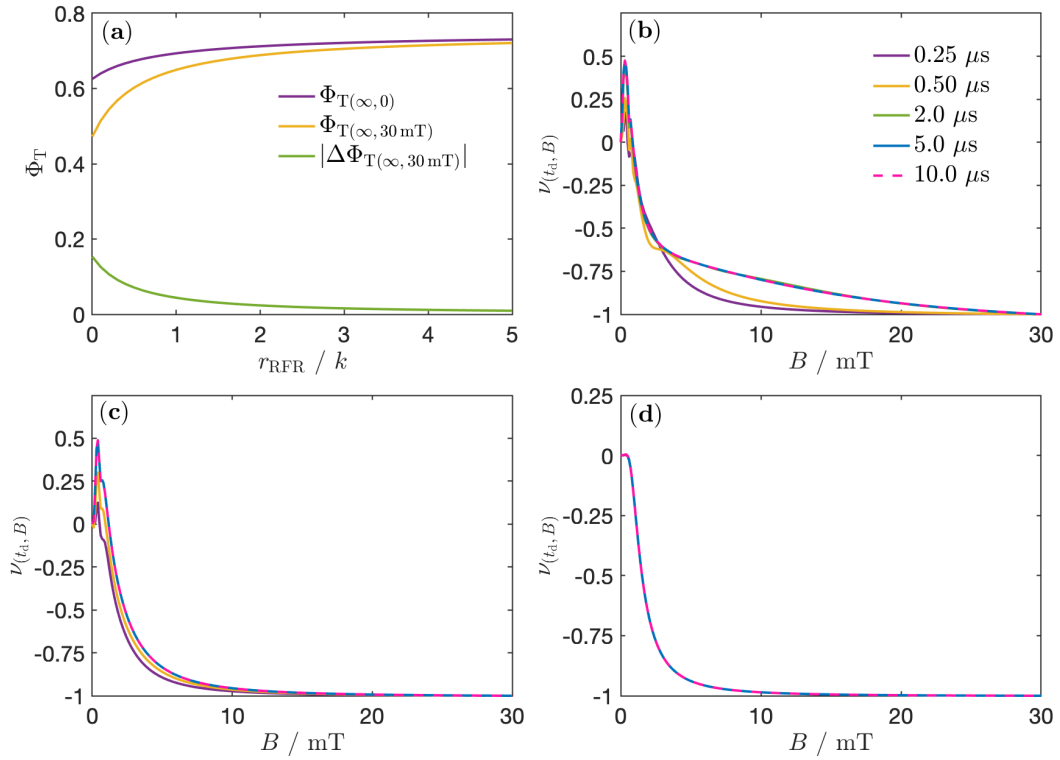


Figure 5.5: Random fields relaxation is considered for the simple radical pair (each radical includes an isotropic nitrogen with the hyperfine parameters, $a_1 = 0.523 \text{ mT}$ and $a_1 = 0.322 \text{ mT}$) with lifetime of $1 \mu\text{s}$. (a) Final triplet yield (i.e. $t_d = \infty$) as a function of the relaxation rate constant (r_{RFR}) relative to the reaction rate constant ($k = 10^6 \text{ s}^{-1}$) for $B = 0$ or 30 mT . $\nu_{(t_d, B)}$ is calculated for three r_{RFR} (b) 5×10^5 , (c) 5×10^6 , (d) $5 \times 10^7 \text{ s}^{-1}$.

within the protein [63]. The RFR superoperator is

$$\hat{W}_{\text{RFR}} = r_{\text{RFR}} \left(\frac{3}{2} \hat{\mathbb{1}} - \sum_{J=1,2} \sum_{i=x,y,z} \hat{S}_{Ji} \otimes \hat{S}_{Ji}^{\text{T}} \right), \quad (5.12)$$

where r_{RFR} is the RFR rate constant, which is difficult to be measured physically at any accuracy, and $J = 1, 2$ denotes the radical. Figure 5.5(a) shows the final triplet yield (i.e. $\Phi_{\text{T}(\infty,0)}$ and $\Phi_{\text{T}(\infty,30\text{ mT})}$ where “ $t_d = \infty$ ” means that the reactions have completed) as a function of r_{RFR}/k . The inclusion of RFR increases the triplet yield even though a strong magnetic field (~ 30 mT) is applied. This is because the RFR relaxes the spin state to equilibrium, disregarding the energy gap between the singlet and triplet states caused by the applied field (i.e. all the populations of the singlet and triplet states head towards $1/4$, and all the spin coherences are annihilated), whereby $\Phi_{\text{T}(\infty,30\text{ mT})}$ intends to become $3/4$. In this sense, the magnetic field effect is destroyed under fast RFR (e.g. $|\Delta\Phi_{\text{T}(\infty,30\text{ mT})}|$ decreases by 50% with $r_{\text{RFR}} \sim 10^6 \text{ s}^{-1}$), shown in Figure 5.5(a). Moreover, Figures 5.5(b), (c) and (d) show $\nu_{(t_d,B)}$ for $r_{\text{RFR}} = 5 \times 10^5$, 5×10^6 and $5 \times 10^7 \text{ s}^{-1}$, and none of them shows appreciable time-dependence of $B_{1/2}$. Thus, we speculate that RFR is not, at least not the only, appropriate spin relaxation mechanism in W369F mutants of Cry4a proteins.

Singlet-triplet dephasing

Singlet-triplet dephasing (STD) can arise from the modulation of the electron exchange interaction brought about by the fluctuation of the inter-radical separation [65]. Remembering the representation of the exchange interaction $\hat{H}_{\text{ex}}$ in equation (2.67) and assuming J to have exponential form as in equation (2.68), we write the fluctuation of $\hat{H}_{\text{ex}}$ as

$$\hat{h}_{\text{ex}(t)} = f_{(t)} \hat{h}_1, \quad (5.13)$$

where $\hat{h}_1 = -(\hat{\mathbb{1}}/2 + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2)$, and $f_{(t)} = J_{(r_{(t)})} - J_{(r_{av})}$ is the stochastic term. Applying Redfield approach with assuming the correlation functions have the form of an exponential decay as in equation (2.103), we obtain the relaxation superoperator for the fluctuation of J as

$$\hat{W}_{\text{STD}} = \tau_c \langle \hat{h}_{\text{ex}(t)} \hat{h}_{\text{ex}(t)} \rangle = \tau_c \langle f_{(t)}^2 \rangle \hat{h}_1^2, \quad (5.14)$$

where the extreme narrowing limit as in equation (2.105) has been used (i.e. $\tau_c^2 \epsilon_{pn}^2 \ll 1$ in which ϵ_{pn} denote the differences between two different energy gaps in Section 2.5.3, Chapter 2), $\hat{h}_1 = \hat{h}_1 \otimes \hat{\mathbb{1}} - \hat{\mathbb{1}} \otimes \hat{h}_1^{\text{T}}$. Note that $\hat{P}^{\text{S}} = \hat{\mathbb{1}}/4 - \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ and $\hat{P}^{\text{T}} = 3\hat{\mathbb{1}}/4 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$, so that $\hat{h}_1 = \hat{P}^{\text{S}} - \hat{P}^{\text{T}}$ and $\hat{h}_1^2 = (\hat{P}^{\text{S}} \otimes \hat{\mathbb{1}} - \hat{\mathbb{1}} \otimes \hat{P}^{\text{S}}) - (\hat{P}^{\text{T}} \otimes \hat{\mathbb{1}} - \hat{\mathbb{1}} \otimes \hat{P}^{\text{T}}) = 2(\hat{P}^{\text{S}} \otimes \hat{P}^{\text{T}} - \hat{P}^{\text{T}} \otimes \hat{P}^{\text{S}})$. Then, $\hat{h}_1^2 = 4(\hat{P}^{\text{S}} \otimes \hat{P}^{\text{T}} + \hat{P}^{\text{T}} \otimes \hat{P}^{\text{S}})$, and $\hat{W}_{\text{STD}}$ can be rewritten,

$$\hat{W}_{\text{STD}} = r_{\text{STD}}(\hat{P}^{\text{S}} \otimes \hat{P}^{\text{T}} + \hat{P}^{\text{T}} \otimes \hat{P}^{\text{S}}), \quad (5.15)$$

where $r_{\text{STD}} = 4\tau_c \langle f_{(t)}^2 \rangle$. Clearly from the representation of STD in equation (5.15), such relaxation mechanism causes decoherence process selectively between the singlet and triplet states. STD has been evoked previously as an explanation for the unexpectedly large $B_{1/2}$ values observed for Cry1 from plant *Arabidopsis thaliana* and DNA photolyase from *E. coli* [53].

Here, we include the STD mechanism in the calculation of $\Delta\Phi_{\text{T}(t_d, 30 \text{ mT})}$. In Figure 5.6(a), in contrast with RFR, STD surprisingly preserves the magnetic field effect (i.e. $\Delta\Phi_{\text{T}(\infty, B)}$), even increases it slightly. It is promising that even with STD much quicker than the reactions, the MFE, which here is defined as $|\Delta\Phi_{\text{T}(\infty, 30 \text{ mT})}|/\Phi_{\text{T}(\infty, 0)}$ meaning the change in triplet yield brought about by the applied magnetic field ($\sim 30 \text{ mT}$) relative to the zero-field triplet yield, can still reach $\sim 20\%$ (Table 5.1). Comparing Figure 5.6(a) with Figure 5.5(a), we find that the distinction between the effects of RFR and STD on $|\Delta\Phi_{\text{T}(\infty, 30 \text{ mT})}|$ is

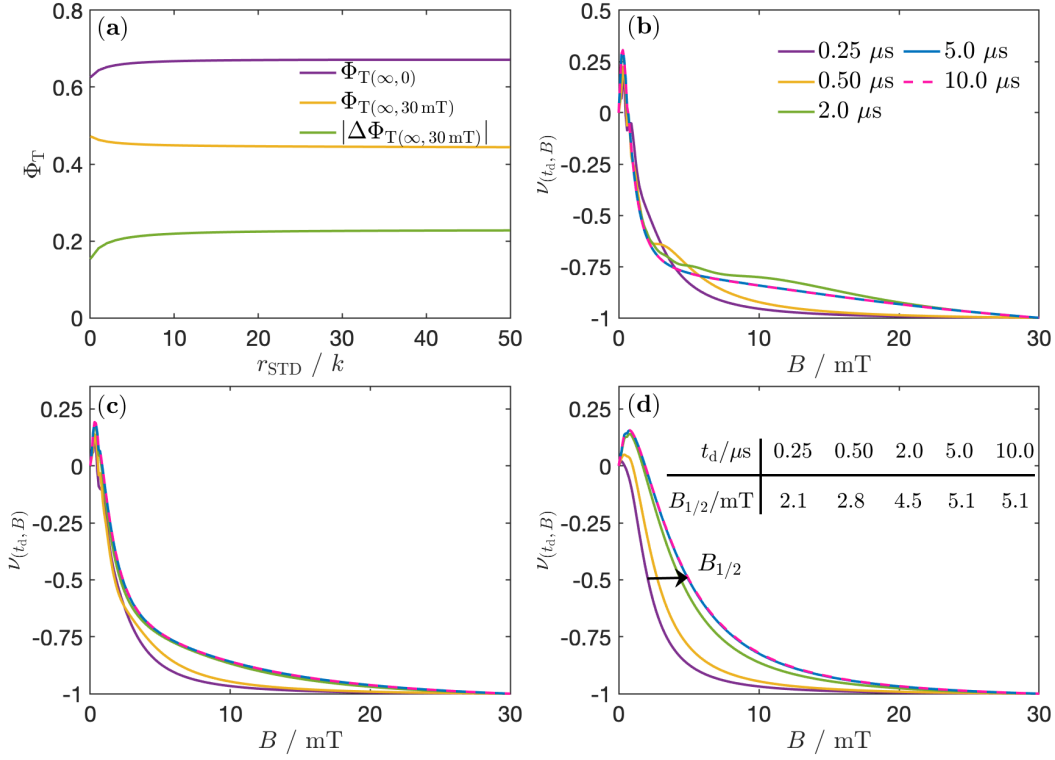


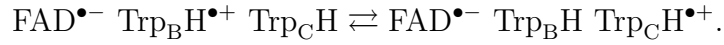
Figure 5.6: Singlet-triplet dephasing is considered for the simple radical pair (each radical includes an isotropic nitrogen with the hyperfine parameters, $a_1 = 0.523$ mT and $a_1 = 0.322$ mT) with lifetime of $1 \mu s$. (a) Final triplet yield (i.e. $t_d = \infty$) as a function of the relaxation rate constant (r_{STD}) relative to the reaction rate constant ($k = 10^6 s^{-1}$) for $B = 0$ or 30 mT. $\nu(t_d, B)$ is calculated for three r_{STD} (b) 5×10^5 , (c) 5×10^6 , (d) $5 \times 10^7 s^{-1}$.

due to their influences on $\Phi_{T(\infty, 30 \text{ mT})}$: the RFR increases $\Phi_{T(\infty, 30 \text{ mT})}$ through non-selectively relaxing the spin state, whereas STD does not change the triplet yield under a strong field ~ 30 mT, meaning that STD seems unable to efficiently relax the spin state towards equilibrium under a high field. Figures 5.6(b), (c) and (d) show $\nu(t_d, B)$ for $r_{STD} = 5 \times 10^5$, 5×10^6 and $5 \times 10^7 s^{-1}$. $B_{1/2}$ does not have a profound time-dependence with r_{STD} below $5 \times 10^6 s^{-1}$, but when r_{STD} reaches $5 \times 10^7 s^{-1}$, $B_{1/2}$ explicitly rises from 2.1 mT to 5.0 mT as the pump-probe delay increases from 0.25 to 10 μs . Therefore, STD potentially accounts for the time-dependence of $B_{1/2}$ in the W369F mutants. However, although $J(r(t))$ is a steep function of the centre-centre separation $r(t)$ that fluctuates within the protein as a

result of thermal motion, the exchange interaction is so small for FAD-Trp_C radical pairs in Cry4a ($< 10 \mu\text{T}$ according to recent electron paramagnetic resonance experiments [79]) that it is very unlikely to be an important source of dephasing.

Electron hopping

The modulation of the exchange interaction does not necessarily rely on the fluctuation of the inter-radical separation - a more credible mechanism is electron hopping between the second (Trp_B) and the third (Trp_C) components of the Trp-triad:



We refer to the states on the left and right hand side as RP_B and RP_C respectively. The rate constant for RP_B $\rightarrow$ RP_C is denoted by k_{BC} , and the rate constant for RP_B $\leftarrow$ RP_C is denoted by k_{CB} . It is suggested that the Trp radical is mostly localized on Trp_CH^{•+} (i.e. $k_{BC} \gg k_{CB}$) [79, 131–133]. Moreover, the FAD^{•−} radical is $\sim 4.6 \text{ \AA}$ closer to Trp_BH^{•+} than to Trp_CH^{•+} [79, 134], giving rise to an exchange interaction as large as $\sim 1 \text{ T}$ in RP_B [93]. The effect of the reversible electron hopping process on the spin dynamics may be seen by a two-site model [135]:

$$\begin{aligned} \frac{d\rho_B}{dt} &= -(i\hat{H}_B + \hat{K}_B)\rho_B - k_{BC}\rho_B + k_{CB}\rho_C, \\ \frac{d\rho_C}{dt} &= -(i\hat{H}_C + \hat{K}_C)\rho_C - k_{CB}\rho_C + k_{BC}\rho_B, \end{aligned} \quad (5.16)$$

where, with $X = B, C$, $\hat{H}_X$ is the Hamiltonian commutation superoperator, $\hat{K}_X$ is the superoperator describing the other chemical reactions (e.g. radical pair recombination). When $k_{BC} \gg k_{CB}$, such that site B returns to site C almost immediately and therefore has a short lifetime and a low equilibrium population, we may neglect $\hat{K}_B$ and use the steady-state approximation in chemical kinetics

$d\rho_B/dt = 0$ [135, 136], to obtain:

$$\rho_B = k_{CB}(i\hat{H}_B + k_{BC}\hat{\mathbb{1}})^{-1}\rho_C. \quad (5.17)$$

Note that in RP_B the exchange interaction far outweighs any other spin magnetic interaction, whereby $\hat{H}_B$ is considered as the commutation superoperator for a strong exchange interaction Hamiltonian. Substituting equation (5.17) into the dynamical equation for ρ_C in equation (5.16), we have:

$$\begin{aligned} \frac{d\rho_C}{dt} &= -(i\hat{H}_C + \hat{K}_C)\rho_C - k_{CB}\rho_C + k_{BC}k_{CB}(i\hat{H}_B + k_{BC}\hat{\mathbb{1}})^{-1}\rho_C \\ &= -(i\hat{H}_C + \hat{K}_C)\rho_C - k_{CB}\left(\hat{\mathbb{1}} - k_{BC}(i\hat{H}_B + k_{BC}\hat{\mathbb{1}})^{-1}\right)\rho_C \\ &= -(i\hat{H}_C + \hat{K}_C)\rho_C - k_{CB}\left((i\hat{H}_B + k_{BC}\hat{\mathbb{1}})(i\hat{H}_B + k_{BC}\hat{\mathbb{1}})^{-1}\right. \\ &\quad \left.- k_{BC}(i\hat{H}_B + k_{BC}\hat{\mathbb{1}})^{-1}\right)\rho_C \\ &= -(i\hat{H}_C + \hat{K}_C)\rho_C - i k_{CB}\hat{H}_B(i\hat{H}_B + k_{BC}\hat{\mathbb{1}})^{-1}\rho_C \\ &= -(i\hat{H}_C + \hat{K}_C + \hat{W})\rho_C, \end{aligned} \quad (5.18)$$

where $\hat{W} = i k_{CB}\hat{H}_B(i\hat{H}_B + k_{BC}\hat{\mathbb{1}})^{-1}$ is the equivalent relaxation superoperator brought about by the electron hopping. In the singlet-triplet basis, the matrix form of $\hat{H}_B$ is

$$\hat{H}_B = \begin{pmatrix} -J_B & 0 \\ 0 & J_B \end{pmatrix}, \quad (5.19)$$

where J_B is the energy for the singlet state and $-J_B$ is the energy for the triplet states. Then, the matrix representation of $\hat{H}_B$ is obtained as:

$$\hat{H}_B = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -2J_B & 0 & 0 \\ 0 & 0 & 2J_B & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (5.20)$$

so that the matrix representation of $\hat{W}$ is

$$\hat{W} = iJ_B k_{CB} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \frac{-1}{-i2J_B + k_{BC}} & 0 & 0 \\ 0 & 0 & \frac{1}{i2J_B + k_{BC}} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (5.21)$$

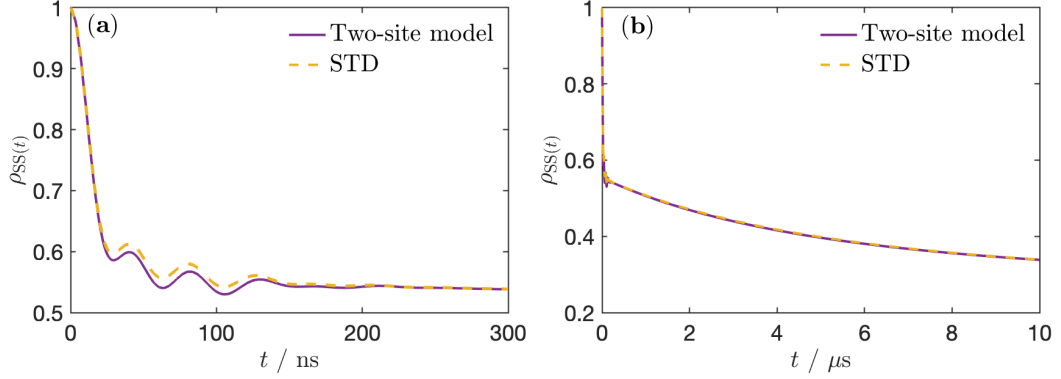


Figure 5.7: Same radical pair for RP_C as that in Figure 5.4 and only the extremely strong (1 T) exchange interaction is considered for RP_B . No recombination reaction is taken into account for RP_B and RP_C (i.e. $\hat{K}_B = \hat{K}_C = 0$). $k_{BC} = 10^{11} \text{ s}^{-1}$ and $k_{CB} = 5 \times 10^7 \text{ s}^{-1}$. “Two-site model”, the exact method in expressing the electron-hopping following equation (5.16), and “STD”, the equivalent spin-relaxation in RP_C method following equation (5.22), are compared ((a) $0 < t < 300 \text{ ns}$ and (b) $0 < t < 10 \mu\text{s}$) by the time-dependent singlet state probability $\rho_{\text{SS}}(t)$ of RP_C .

Hence, $\hat{W}$ adds a singlet-triplet dephasing term $\hat{W}_{\text{STD}}$ and an additional exchange interaction term $\hat{H}'_{\text{ex}}$ to the time-dependence of ρ_C : $\hat{W} = \hat{W}_{\text{STD}} + i\hat{H}'_{\text{ex}}$, where

$$\begin{aligned}\hat{W}_{\text{STD}} &= r_{\text{STD}}(\hat{P}^S \otimes \hat{P}^T + \hat{P}^T \otimes \hat{P}^S), \\ \hat{H}'_{\text{ex}} &= -2J'_{\text{ex}}(\hat{P}^T \otimes \hat{P}^S - \hat{P}^S \otimes \hat{P}^T),\end{aligned}\tag{5.22}$$

in which

$$r_{\text{STD}} = \frac{4J_B^2 k_{CB}}{4J_B^2 + k_{BC}^2}, \quad J'_{\text{ex}} = \frac{J_B k_{CB} k_{BC}}{4J_B^2 + k_{BC}^2}.\tag{5.23}$$

Reliable experimental measurements of k_{BC} , k_{CB} and J_B are not available. If $J_B \gg k_{BC}$, then equation (5.23) gives $r_{\text{STD}} \approx k_{CB}$, supporting the estimation of r_{STD} in Ref [53] at the order of 10^7 s^{-1} . In the same limit, $J'_{\text{ex}} \ll k_{CB}$, implying a negligible effect on the spin dynamics. The equivalent STD and additional exchange interaction is verified through the comparison of the time-dependent singlet state probability $\rho_{\text{SS}}(t)$ of RP_C from equations (5.22) and (5.23) with that from the exact two-site model in equation (5.16). In Figure 5.7, $\rho_{\text{SS}}(t)$ for the “STD” method satisfactorily matches that for the exact method throughout the spin dynamics time period (i.e. $t < 10 \mu\text{s}$). Therefore, singlet-triplet dephasing

induced by the electron hopping between RP_B and RP_C is realistic.

Triplet-triplet dephasing

The fluctuation of the centre-centre separation can also lead to the stochastic modulation of the electronic dipolar interaction written [65],

$$\hat{h}_{\text{dip}} = g(t) \hat{h}_2, \quad (5.24)$$

where

$$\hat{h}_2 = \frac{2}{3}(3\hat{S}_{1z}\hat{S}_{2z} - \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2) = \frac{1}{3}\hat{P}^{\text{T}+} + \frac{1}{3}\hat{P}^{\text{T}-} - \frac{2}{3}\hat{P}^{\text{T}0},$$

and $g(t) = D(r(t)) - D(r_{\text{av}})$ characterizes the modulation of the strength of the dipolar

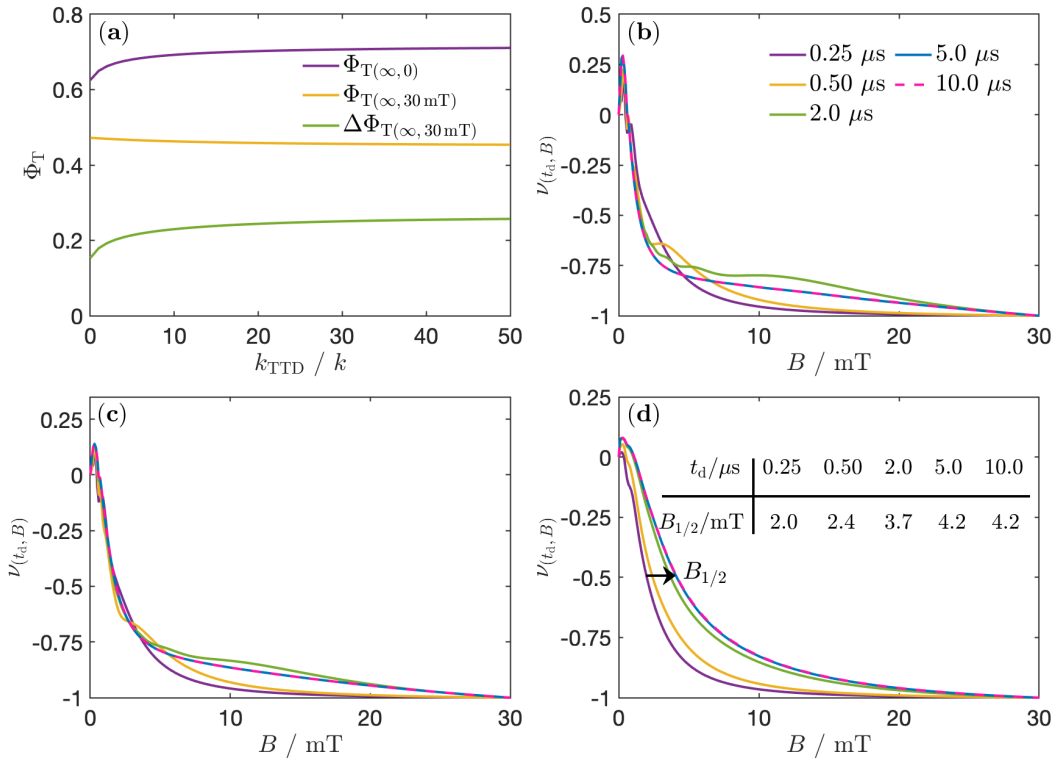


Figure 5.8: Triplet-triplet dephasing is considered for the simple radical pair (each radical includes an isotropic nitrogen with the hyperfine parameters, $a_1 = 0.523$ mT and $a_1 = 0.322$ mT) with lifetime of $1 \mu\text{s}$. (a) Final triplet yield (i.e. $t_d = \infty$) as a function of the relaxation rate constant (r_{TTD}) relative to the reaction rate constant ($k = 10^6 \text{ s}^{-1}$) for $B = 0$ or 30 mT. $\nu(t_d, B)$ is calculated for three r_{TTD} (b) 5×10^5 , (c) 5×10^6 , (d) $5 \times 10^7 \text{ s}^{-1}$.

interaction. Such D -modulation gives rise to triplet-triplet dephasing (TTD). Applying Redfield approach with extreme narrowing limit, the superoperator of TTD is obtained as [65]

$$\begin{aligned}\hat{W}_{\text{TTD}} &= \tau_c \langle g_{(t)}^2 \rangle \hat{h}_2^2 \\ &= r_{\text{TTD}} \left(\frac{1}{9} \hat{P}^S \otimes \hat{P}^{T+} + \frac{1}{9} \hat{P}^{T+} \otimes \hat{P}^S + \frac{1}{9} \hat{P}^S \otimes \hat{P}^{T-} + \frac{1}{9} \hat{P}^{T-} \otimes \hat{P}^S \right. \\ &\quad + \frac{4}{9} \hat{P}^S \otimes \hat{P}^{T_0} + \frac{4}{9} \hat{P}^{T_0} \otimes \hat{P}^S + \hat{P}^{T+} \otimes \hat{P}^{T_0} + \hat{P}^{T_0} \otimes \hat{P}^{T+} \\ &\quad \left. + \hat{P}^{T-} \otimes \hat{P}^{T_0} + \hat{P}^{T_0} \otimes \hat{P}^{T-} \right),\end{aligned}\tag{5.25}$$

where $r_{\text{TTD}} = \tau_c \langle g_{(t)}^2 \rangle$ is the triplet-triplet dephasing rate constant. In $\hat{W}_{\text{TTD}}$, not only the coherences between the singlet and triplet states but also those among the triplet states are relaxed. In Figure 5.8(a), we see that TTD also preserves $\Delta\Phi_{T(\infty, B)}$. $B_{1/2}$ explicitly rises by time on condition that $r_{\text{TTD}} \gtrsim 10^7 \text{ s}^{-1}$ (Figures 5.8(b), (c) and (d)). However, although the dipolar interaction ($\sim -470 \text{ } \mu\text{T}$) is much stronger than the exchange interaction in the FAD-Trp_C radical pair [79], this does not necessarily mean that the triplet-triplet dephasing can probably be as fast as $\sim 10^7 \text{ s}^{-1}$, as $D_{(r)}$ has a much weaker dependence on the inter-radical separation than $J_{(r)}$. Assume that the inter-radical separation is in a Gaussian distribution, centred at $r = r_{\text{av}}$, with the standard deviation σ_r :

$$\mathcal{P}_{(r)} = \frac{1}{\sigma_r \sqrt{2\pi}} e^{-\frac{(r - r_{\text{av}})^2}{2\sigma_r^2}}.\tag{5.26}$$

Using $\sigma_r = 0.1 \text{ nm}$, $r_{\text{av}} = 1.85 \text{ nm}$ [79] and $\tau_c = 0.1 \text{ ns}$, r_{TTD} is obtained as

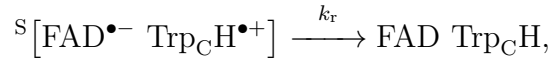
$$r_{\text{TTD}} = \tau_c \langle g_{(t)}^2 \rangle = \tau_c \int_0^\infty \mathcal{P}_{(r)} (D_{(r(t))} - D_{(r_{\text{av}})})^2 dr = 1.7 \times 10^5 \text{ s}^{-1}.\tag{5.27}$$

Such slow TTD is very unlikely to induce any time-dependence of $B_{1/2}$.

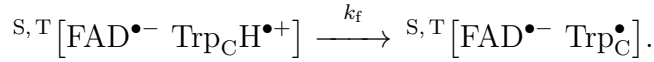
5.1.2 Exact modelling

The analysis of the time-dependence of $B_{1/2}$ in Section 5.1.1 is approximate because it assumes that singlet and triplet radical pairs react spin selectively to

give distinct singlet and triplet products with equal rate constants. The reality is that there is no accessible triplet product state of cryptochrome that could be formed spin-selectively from the triplet radical pair [53, 79]. A more realistic modelling must follow the reaction scheme in Figure 5.3, which consists of a spin-selective recombination of singlet radical pairs to the ground state of the protein (rate constant k_r),



and a competitive spin-independent deprotonation of the tryptophan radical (rate constant k_f),



Now, the chemical reaction superoperator is

$$\hat{K} = \frac{k_r}{2}(\hat{P}^S \otimes \hat{\mathbb{1}} + \hat{\mathbb{1}} \otimes \hat{P}^S) + k_f \hat{\mathbb{1}}, \quad (5.28)$$

where the projection operator for the forward reaction (i.e. the deprotonation of $\text{Trp}_C\text{H}^{\bullet+}$) is the identity matrix, $\hat{P}^F = \hat{\mathbb{1}}$, its vectorised form in Liouville space is denoted by σ^F .

The hyperfine interactions of the electron with multiple nuclear spins are treated by a simple semi-classical approximation proposed by Schulten and Wolynes [137]. This approximation neglects the (comparatively slow) nuclear spin evolution and replaces the nuclear spin operators by classical field vectors:

$$a_{Jk} \hat{\mathbf{I}}_{Jk} \Longrightarrow \mathbf{h}_{Jk}, \quad (5.29)$$

where $\hat{\mathbf{I}}_{Jk}$ is the k -th nuclear spin operator in radical J, a_{Jk} is its isotropic hyperfine constant, and $\mathbf{h}_{Jk} = (h_{Jk}^x, h_{Jk}^y, h_{Jk}^z)^\top$ is the hyperfine field. Note that although equation (5.29) destroys the (nearly) degenerate spin subspaces which are

significant for the low field effect [54, 104], this semi-classical method is reasonably reliable for the modelling of the time-dependent magnetic field effect here with applied fields stronger than the internal hyperfine interactions. $\mathbf{h}_{Jk}$ is randomly oriented and

$$|\mathbf{h}_{Jk}| = \sqrt{a_{Jk}^2 I_{Jk}(I_{Jk} + 1)}, \quad (5.30)$$

where I_{Jk} denotes the nuclear spin quantum number, so that

$$\sum_{\alpha=x,y,z} (h_{Jk}^\alpha)^2 = |\mathbf{h}_{Jk}|^2 = a_{Jk}^2 I_{Jk}(I_{Jk} + 1). \quad (5.31)$$

Assuming that h_{Jk}^α is a random variable with the mean value $\mu_{Jk} = 0$ and the variance given by $\sigma_{Jk}^2 = a_{Jk}^2 I_{Jk}(I_{Jk} + 1)/3$, the summed component hyperfine field in a radical, $h_J^\alpha = \sum_k h_{Jk}^\alpha$, thus tends towards a normal distribution, according to Lyapunov central limit theorem [138]:

$$\mathcal{P}_{(h_J^\alpha)} = \frac{1}{\sigma_J \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{h_J^\alpha}{\sigma_J} \right)^2}, \quad (5.32)$$

where the standard deviation σ_J is equal to the effective isotropic hyperfine interaction constant in equation (5.3). The multiple nuclear spins in the radical pair allow us to apply the central limit theorem. Hence, the probability of the summed hyperfine field $\mathbf{h}_J$, with its strength $|\mathbf{h}_J| = \sqrt{(h_J^x)^2 + (h_J^y)^2 + (h_J^z)^2}$, is

$$\mathcal{P}_{(\mathbf{h}_J)} = (\mathcal{P}_{(h_J^\alpha)})^3 = \left(\frac{1}{2\pi\sigma_J^2} \right)^{3/2} e^{-\frac{1}{2} \left(\frac{|\mathbf{h}_J|}{\sigma_J} \right)^2}, \quad (5.33)$$

which was appropriately used to characterize the internal magnetic fields (induced by hyperfine interactions) in a radical pair in previous works [139, 140]. Thus, the spin magnetic Hamiltonian for the FAD-Trp_C radical pair is written,

$$\hat{H}_{SW} = \boldsymbol{\omega}_1 \cdot \hat{\mathbf{S}}_1 + \boldsymbol{\omega}_2 \cdot \hat{\mathbf{S}}_2, \quad (5.34)$$

where $\boldsymbol{\omega}_J = \mathbf{h}_J - \gamma_e B \mathbf{n}_z$ in which $\mathbf{n}_z$ is the unit vector along the z -axis. Note that both the exchange interaction (too small) and the electronic dipolar interaction

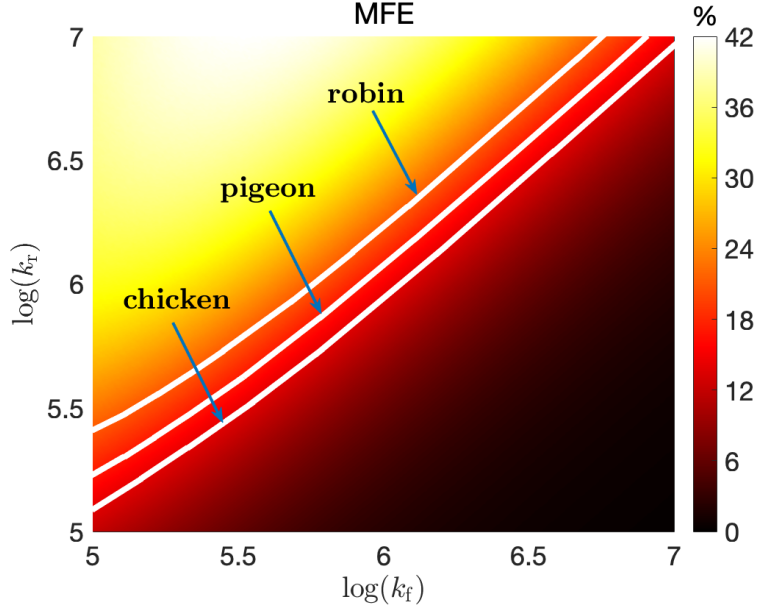


Figure 5.9: Schulten-Wolynes semi-classical calculation of the MFE for the FAD-Trp_C radical pair with singlet-triplet dephasing. k_r and k_f vary in the range 10^5 - 10^7 s⁻¹. $B = 30$ mT and $r_{\text{STD}} = 3.5 \times 10^7$ s⁻¹.

(assumed to be averaged out in solution) are ignored. In the spin dynamics modelling, the effect of hyperfine fields on the spin dynamics is included by averaging over the normal distributions of hyperfine fields in equation (5.32) (using 10^4 Monte Carlo samples).

Considering the MFE $\sim 20\%$ and the time-dependent $B_{1/2}$, we adopt the singlet-triplet dephasing as the sole spin relaxation mechanism in the spin dynamics modelling. Then, the Liouvillian superoperator is

$$\hat{\hat{L}}_{\text{SW}} = i\hat{\hat{H}}_{\text{SW}} + \hat{\hat{K}} + \hat{\hat{W}}_{\text{STD}}. \quad (5.35)$$

The time-dependent recombination yield $\Phi_{\text{r}(t_d, B)}$ and forward reaction yield $\Phi_{\text{f}(t_d, B)}$ are obtained as

$$\begin{aligned} \Phi_{\text{r}(t_d, B)} &= \langle k_r \int_0^{t_d} (\hat{\sigma}^{\text{S}})^{\text{T}} \sigma_{(t)} dt \rangle = \langle \frac{k_r}{Z} (\hat{\sigma}^{\text{S}})^{\text{T}} (\hat{\hat{L}}_{\text{SW}})^{-1} (\hat{\mathbb{1}} - e^{-\hat{\hat{L}}_{\text{SW}} t_d}) \hat{\sigma}^{\text{S}} \rangle, \\ \Phi_{\text{f}(t_d, B)} &= \langle k_f \int_0^{t_d} (\hat{\sigma}^{\text{F}})^{\text{T}} \sigma_{(t)} dt \rangle = \langle \frac{k_f}{Z} (\hat{\sigma}^{\text{F}})^{\text{T}} (\hat{\hat{L}}_{\text{SW}})^{-1} (\hat{\mathbb{1}} - e^{-\hat{\hat{L}}_{\text{SW}} t_d}) \hat{\sigma}^{\text{S}} \rangle, \end{aligned} \quad (5.36)$$

	robin	chicken	pigeon
$k_r/10^5 \text{ s}^{-1}$	9.3	5.8	8.7
$k_f/10^5 \text{ s}^{-1}$	5.4	6.5	7.4
$r_{\text{STD}}/10^7 \text{ s}^{-1}$	3.2	2.4	6.1

Table 5.3: Fitted rate constants for the (singlet) recombination (k_r), the spin-independent deprotonation (k_f) of $\text{Trp}_\text{C}\text{H}^{\bullet+}$ and STD (r_{STD}) in the $[\text{FAD}^{\bullet-} \text{Trp}_\text{C}\text{H}^{\bullet+}]$ radical pair.

where $\langle \dots \rangle$ means the average over the sample of hyperfine fields, and the final yields are:

$$\begin{aligned}\Phi_{\text{r}(\infty, B)} &= \left\langle \frac{k_r}{Z} (\hat{\sigma}^{\text{S}})^\top (\hat{L}_{\text{SW}})^{-1} \hat{\sigma}^{\text{S}} \right\rangle, \\ \Phi_{\text{f}(\infty, B)} &= \left\langle \frac{k_f}{Z} (\hat{\sigma}^{\text{F}})^\top (\hat{L}_{\text{SW}})^{-1} \hat{\sigma}^{\text{S}} \right\rangle.\end{aligned}\tag{5.37}$$

Regarding that the extinction coefficient of the ground state (recombination product) at 530 nm is zero [129], $\text{MFE} = |\Delta\Phi_{\text{f}(\infty, 30 \text{ mT})}/\Phi_{\text{f}(\infty, 0)}|$ is equivalent to that in Table 5.1 for the three mutants of avian Cry4a proteins (robin 21%, chicken 14% and pigeon 17%). Note that STD with $r_{\text{STD}} \gtrsim 10k = 10^7 \text{ s}^{-1}$ does not affect the yields of reaction products (Figure 5.6(a)). Therefore, the assignment of the value of r_{STD} is not limited at the goal of finding the appropriate k_r and k_f to satisfy the experimental MFE and fitting the chemical kinetics characterized by t_1 in Table 5.1. Taking $k_{\text{STD}} = 3.5 \times 10^7 \text{ s}^{-1}$, we calculate $\Phi_{\text{f}(\infty, 0)}$ and $\Phi_{\text{f}(\infty, 30 \text{ mT})}$ with k_b and k_f both in the range 10^5 - 10^7 s^{-1} . The corresponding MFE (in the range $0 < \text{MFE} < 42\%$) is shown in Figure 5.9. The regions in which the MFE agree with those in Table 5.1 are denoted by the three white lines, where the proper k_r and k_f corresponding to the chemical kinetics represented by t_1 in Table 5.1 will be found. The extinction coefficients of $\text{Trp}_\text{C}\text{H}^{\bullet+}$ and $\text{Trp}_\text{C}^\bullet$ at 530 nm are known to be similar [129], and for simplicity we assume they are equal. The extinction coefficient of the ground state at 530 nm is zero [129]. Therefore, the time-dependent change in absorbance in Figure 5.1(a) describes the remaining $[\text{FAD}^{\bullet-} \text{Trp}_\text{C}\text{H}^{\bullet+}]$ radical pairs ($\Phi_{\text{RPC}(t_d, 0)}$) and the accumulation of $\text{FAD}^{\bullet-} \text{Trp}_\text{C}^\bullet$

5.1. Spin dynamics modelling

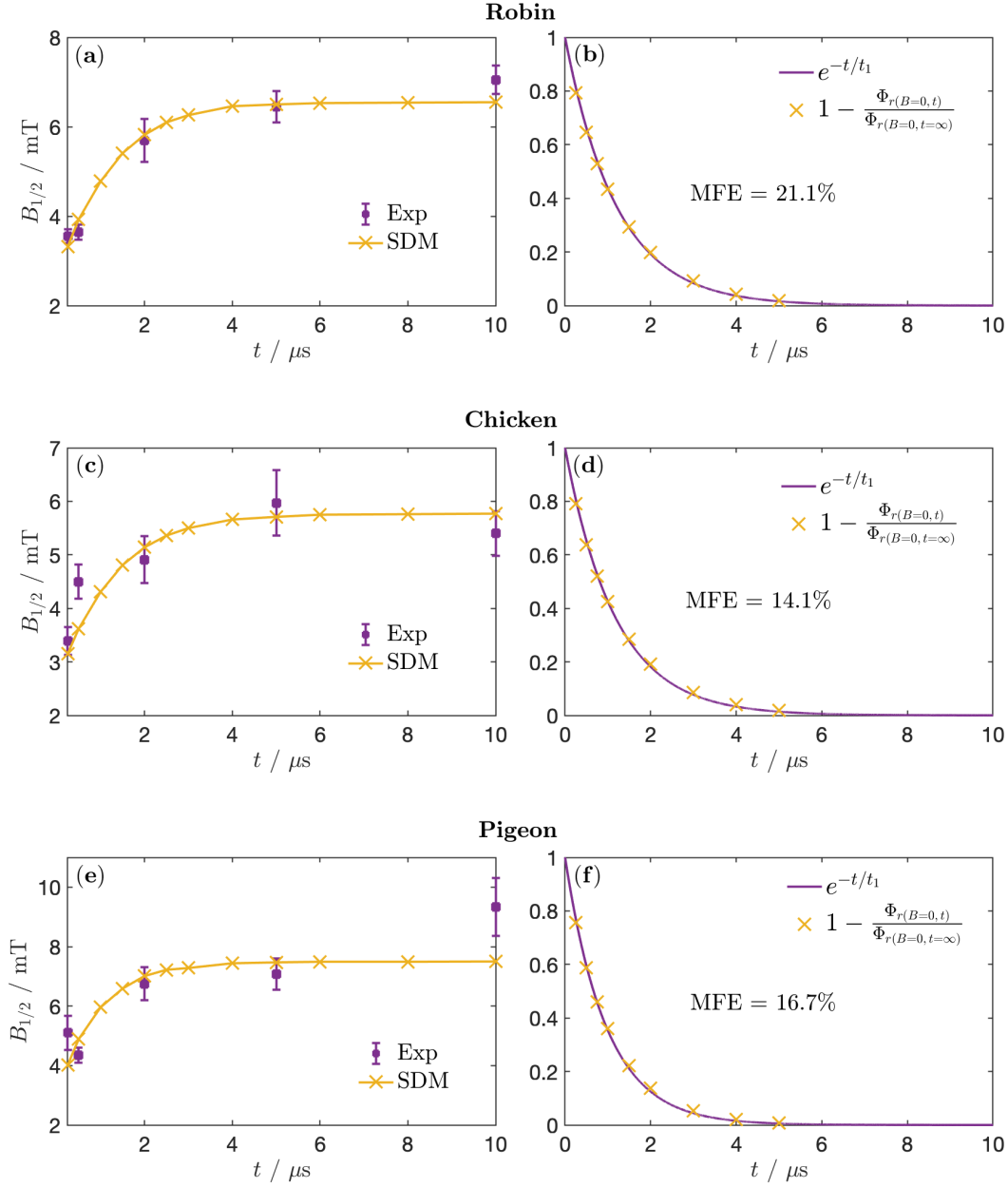


Figure 5.10: Exact spin dynamics modelling of W369F mutants of the three avian (robin, chicken and pigeon) Cry4a proteins. (a), (c) and (e) show the fitting of the time-dependent $B_{1/2}$ (“Exp” denote the experimental data and “SDM” means spin dynamics modelling). (b), (d) and (f) show the fitting of k_r and k_f to the chemical kinetics t_1 in Table 5.1, and the corresponding MFE is also noted.

$(\Phi_{f(t_d, 0)})$ at zero field. Thus, t_1 characterizes the kinetics of the time-dependent yield of recombination $(\Phi_{r(t_d, 0)})$ remembering that $\Phi_{\text{RPC}(t_d, 0)} + \Phi_{f(t_d, 0)} + \Phi_{r(t_d, 0)} = 1$. This means that $(1 - \Phi_{r(t_d, 0)}/\Phi_{r(\infty, 0)})$ needs to be fit to $\exp(-t_d/t_1)$. The fit k_r

and k_f for robin, chicken and pigeon are shown in Table 5.3. Using them, we vary r_{STD} so as to obtain the $B_{1/2(t_d)}$ values that fit those in Table 5.2. Note that here $B_{1/2}$ is defined as:

$$\begin{aligned} & (\Phi_{\text{RPC}}(t_d, B_{1/2}) + \Phi_{\text{f}}(t_d, B_{1/2})) - (\Phi_{\text{RPC}}(t_d, 0) + \Phi_{\text{f}}(t_d, 0)) \\ &= \frac{(\Phi_{\text{RPC}}(t_d, 30 \text{ mT}) + \Phi_{\text{f}}(t_d, 30 \text{ mT})) - (\Phi_{\text{RPC}}(t_d, 0) + \Phi_{\text{f}}(t_d, 0))}{2}, \end{aligned} \quad (5.38)$$

equivalently:

$$\Phi_{\text{r}(t_d, B_{1/2})} = \frac{\Phi_{\text{r}(t_d, 0)} + \Phi_{\text{r}(t_d, 30 \text{ mT})}}{2}. \quad (5.39)$$

The fitted r_{STD} are obtained in the least square sense (Table 5.3: robin $3.2 \times 10^7 \text{ s}^{-1}$, chicken $2.4 \times 10^7 \text{ s}^{-1}$ and pigeon $6.1 \times 10^7 \text{ s}^{-1}$). Figures 5.10(a), (c) and (e) show the comparison of the $B_{1/2(t_d)}$ from the spin dynamics modelling with the experimental ones - the inclusion of singlet-triplet dephasing succeeds to depict the time-dependent magnetic field effects. Furthermore, one may wonder whether the change of r_{STD} (note that the k_r and k_f in Table 5.3 are obtained with assuming $r_{\text{STD}} = 3.5 \times 10^7 \text{ s}^{-1}$) makes a difference to the chemical kinetics and MFE. However, Figures 5.10(b), (d) and (f) clearly show that k_b and k_f in Table 5.3 still satisfy the t_1 kinetics and the corresponding MFE, even though r_{STD} changes.

5.2 Origin of the time-dependence of $B_{1/2}$

Roughly speaking, a decoherence process as fast as $\sim 0.1 \mu\text{s}^{-1}$ was supposed to completely relax the coherent spin states before the much slower chemical reactions ($\sim 1 \mu\text{s}^{-1}$) can happen. Then, for times longer than $1 \mu\text{s}$, the time-dependence of the magnetic field effects should not emerge. However, singlet-triplet dephasing indeed grants $B_{1/2}$ with a time-dependence till $t_d \lesssim 10 \mu\text{s}$ for the Trp_D mutant cryptochromes of the three avian species. Thus, it is necessary to find out the physics behind. Insights into the effects of spin relaxation on the spin dynamics of

radical pairs considered here can be obtained by reducing the four electron spin states (S, T_0 , T_+ and T_-) to a two-level system. Despite the gross simplifications involved, this “toy” model (inspired by and developed from Maeda *et al.* [140]) reveals how spin relaxation affects the sensitivity of the radical pair reactions to an external magnetic field.

5.2.1 S- T_0 interconversion

The spin Hamiltonian for the two-level S- T_0 radical pair is:

$$\hat{H} = \begin{pmatrix} 0 & q/2 \\ q/2 & 0 \end{pmatrix}, \quad (5.40)$$

where q characterizes the hyperfine interaction. Note that the external magnetic field along the z -axis does not cause extra energy level splitting between the S and T_0 states, so that $H_{SS} = H_{T_0T_0} = 0$. Ignoring the chemical reactions and spin relaxation, the difference between the time-dependent S and T_0 fractions, $\rho_{SS}(t) - \rho_{T_0T_0}(t)$, for a radical pair formed in the S state, is given exactly by:

$$\rho_{SS}(t) - \rho_{T_0T_0}(t) = \cos(qt), \quad (5.41)$$

i.e. the S- T_0 will be sufficiently mixed with the oscillation frequency q . Including singlet-triplet dephasing, the master equation for the density matrix is

$$\frac{d\rho}{dt} = -i[\hat{H}, \rho] - r[\hat{P}^S \rho \hat{P}^{T_0} + \hat{P}^{T_0} \rho \hat{P}^S], \quad (5.42)$$

where $r = r_{STD}$, and the singlet and triplet projection operators are

$$\hat{P}^S = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \hat{P}^{T_0} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

Equation (5.42) can be recast as

$$\frac{d\sigma}{dt} = -\hat{L}\sigma, \quad (5.43)$$

where $\sigma = (\rho_{SS}, \rho_{ST_0}, \rho_{T_0S}, \rho_{T_0T_0})^\top$ with $\top$ = transpose and the matrix representation of the Liouvillian superoperator is

$$\begin{aligned}\hat{L} &= i(\hat{H} \otimes \hat{1} - \hat{1} \otimes \hat{H}^\top) + r(\hat{P}^S \otimes \hat{P}^{T_0} + \hat{P}^{T_0} \otimes \hat{P}^S) \\ &= \frac{1}{2} \begin{pmatrix} 0 & -iq & iq & 0 \\ -iq & 2r & 0 & iq \\ iq & 0 & 2r & -iq \\ 0 & iq & -iq & 0 \end{pmatrix}.\end{aligned}\quad (5.44)$$

Defining σ'

$$\sigma' = \begin{pmatrix} \rho_{ST_0} + \rho_{T_0S} \\ -i(\rho_{ST_0} - \rho_{T_0S}) \\ \rho_{SS} - \rho_{T_0T_0} \\ \rho_{SS} + \rho_{T_0T_0} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & -i & i & 0 \\ 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \rho_{SS} \\ \rho_{ST_0} \\ \rho_{T_0S} \\ \rho_{T_0T_0} \end{pmatrix} = A\sigma \quad (5.45)$$

allows us to rewrite equation (5.43) as

$$\frac{d\sigma'}{dt} = -A\hat{L}A^{-1}\sigma' = -\begin{pmatrix} r & 0 & 0 & 0 \\ 0 & r & -q & 0 \\ 0 & q & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \sigma'. \quad (5.46)$$

Dropping the constant $\rho_{SS} + \rho_{T_0T_0} = 1$ term gives:

$$p = \begin{pmatrix} \rho_{ST_0} + \rho_{T_0S} \\ -i(\rho_{ST_0} - \rho_{T_0S}) \\ \rho_{SS} - \rho_{T_0T_0} \end{pmatrix}; \quad (5.47)$$

$$\frac{dp}{dt} = -\hat{\mathcal{K}}p \Rightarrow p_{(t)} = e^{-\hat{\mathcal{K}}t}p_{(0)}.$$

where

$$\hat{\mathcal{K}} = \begin{pmatrix} r & 0 & 0 \\ 0 & r & -q \\ 0 & q & 0 \end{pmatrix}. \quad (5.48)$$

For a radical pair pair formed at $t = 0$ in a pure singlet state: $p_{(0)} = (0, 0, 1)^\top$.

The eigenvalues of $\hat{\mathcal{K}}$ are

$$\begin{aligned}v_1 &= r, \\ v_2 &= \frac{r + \sqrt{r^2 - 4q^2}}{2}, \\ v_3 &= \frac{r - \sqrt{r^2 - 4q^2}}{2}.\end{aligned}\quad (5.49)$$

The corresponding eigenvectors are the columns of the matrix,

$$V = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{r + \sqrt{r^2 - 4q^2}}{2q} & \frac{r - \sqrt{r^2 - 4q^2}}{2q} \\ 0 & 1 & 1 \end{pmatrix}, \quad (5.50)$$

and its inverse is:

$$V^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{q}{\sqrt{r^2 - 4q^2}} & \frac{-r + \sqrt{r^2 - 4q^2}}{2\sqrt{r^2 - 4q^2}} \\ 0 & \frac{-q}{\sqrt{r^2 - 4q^2}} & \frac{r + \sqrt{r^2 - 4q^2}}{2\sqrt{r^2 - 4q^2}} \end{pmatrix}. \quad (5.51)$$

Using equation (5.47),

$$p(t) = V e^{-\Lambda t} V^{-1} p(0), \quad (5.52)$$

where Λ is the diagonal matrix of the eigenvalues of $\hat{\mathcal{K}}$ in equation (5.48). Combining equations (5.47)-(5.52) gives

$$\begin{aligned} p_3(t) &= \rho_{SS}(t) - \rho_{T_0 T_0}(t) \\ &= \frac{1}{2} e^{-\frac{rt}{2}} \left(\left(1 + \frac{1}{\sqrt{1 - \xi^2}}\right) e^{\frac{\sqrt{1 - \xi^2} r t}{2}} + \left(1 - \frac{1}{\sqrt{1 - \xi^2}}\right) e^{-\frac{\sqrt{1 - \xi^2} r t}{2}} \right), \end{aligned} \quad (5.53)$$

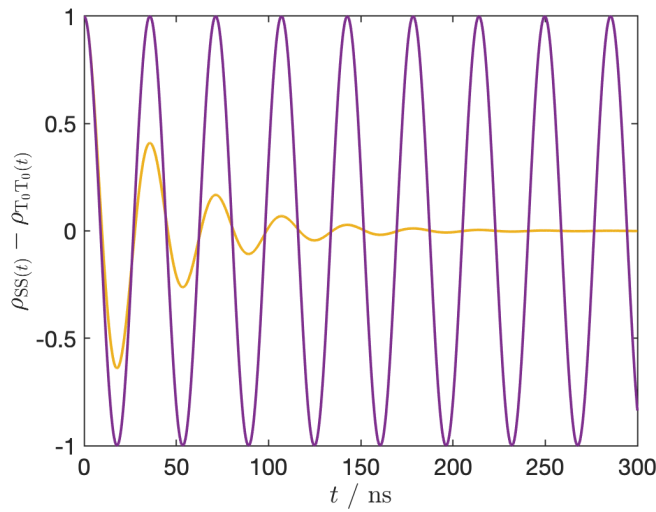


Figure 5.11: Time-dependent population difference between S and T_0 states with (the orange trace) and without (the purple line) singlet-triplet dephasing $r_{STD} = 5 \times 10^7 \text{ s}^{-1}$. Radical reactions are not included. $q = 1 \text{ mT}$.

where $\xi^2 = 4q^2/r^2$. For the FAD-Trp radical pair formed in cryptochromes, q is of the order of 1 mT and r is of the order of 10^7 s^{-1} . Thus, $\xi^2 \gg 1$ (e.g. let $q = 1 \text{ mT}$ and $r = 5 \times 10^7 \text{ s}^{-1}$, then $\xi^2 \approx 49.6$). Therefore, equation (5.53) can be further simplified as

$$\begin{aligned} \rho_{\text{SS}(t)} - \rho_{\text{T}_0\text{T}_0(t)} &= e^{-\frac{r}{2}t} \left(\frac{1}{\sqrt{\xi^2 - 1}} \sin\left(\frac{\sqrt{\xi^2 - 1}}{2} r t\right) + \cos\left(\frac{\sqrt{\xi^2 - 1}}{2} r t\right) \right) \\ &\approx e^{-\frac{r}{2}t} \left(\frac{r}{2q} \sin(q t) + \cos(q t) \right). \end{aligned} \quad (5.54)$$

The STD mechanism damps the S- T_0 interconversion rapidly with the rate constant $r/2$ (Figure 5.11). The radical pair lifetime is $\sim 1 \mu\text{s}$, so that $\rho_{\text{SS}(t)} - \rho_{\text{T}_0\text{T}_0(t)}$ has already decayed to zero before the radical pair reacts. Therefore, the time-dependence of $B_{1/2}$ in the range of several microseconds should not rely on the effect of STD on the S- T_0 interconversion.

5.2.2 S- $\text{T}_{\pm}$ interconversion

Still using the two-level model, the matrix representation of the spin Hamiltonian for the S- T_+ radical pair is:

$$\hat{H} = \begin{pmatrix} 0 & q/2 \\ q/2 & \omega \end{pmatrix}, \quad (5.55)$$

i.e. $H_{\text{SS}} = 0$, $H_{\text{T}_+\text{T}_+} = \omega$, and $H_{\text{ST}_+} = H_{\text{T}_+\text{S}} = q/2$. ω and q play the roles of Zeeman and hyperfine interactions respectively. Note that the energy splitting introduced by the external magnetic field between S and T_+ is equal to that between S and T_- . Thus, the interconversion between S and T_+ is identical to that between S and T_- . Ignoring the chemical reactions and spin relaxation, the difference between the time-dependent S and T_+ fractions, $\rho_{\text{SS}(t)} - \rho_{\text{T}_+\text{T}_+(t)}$, for a radical pair formed in the S state, is given exactly by

$$\rho_{\text{SS}(t)} - \rho_{\text{T}_+\text{T}_+(t)} = \frac{\omega^2 + q^2 \cos(\sqrt{\omega^2 + q^2} t)}{\omega^2 + q^2}. \quad (5.56)$$

When the Zeeman interaction greatly exceeds the hyperfine interactions ($\omega \gg q$), S- T_+ mixing is inefficient and the singlet probability remains close to 1, i.e. the

population difference has a time-independent $\omega^2/(\omega^2 + q^2) \approx 1$ and an oscillatory component of low-amplitude, $q^2/(\omega^2 + q^2)$, and frequency, $\sqrt{\omega^2 + q^2} \approx \omega$.

Including STD, the matrix representation of the Liouvillian superoperator is

$$\hat{L} = \frac{1}{2} \begin{pmatrix} 0 & -iq & iq & 0 \\ -iq & 2(r + i\omega) & 0 & iq \\ iq & 0 & 2(r - i\omega) & -iq \\ 0 & iq & -iq & 0 \end{pmatrix}. \quad (5.57)$$

In analogy with equations (5.43)-(5.45), the specially defined p in Liouville space is

$$p = \begin{pmatrix} \rho_{ST+} + \rho_{T+S} \\ -i(\rho_{ST+} - \rho_{T+S}) \\ \rho_{SS} - \rho_{T+T+} \end{pmatrix}, \quad (5.58)$$

and its dynamical equation is

$$\frac{dp}{dt} = -\hat{\mathcal{K}} p \Rightarrow p(t) = e^{-\hat{\mathcal{K}}t} p_{(0)}, \quad (5.59)$$

where

$$\hat{\mathcal{K}} = \hat{\mathcal{M}} + \hat{\mathcal{Q}}; \quad \hat{\mathcal{M}} = \begin{pmatrix} r & -\omega & 0 \\ \omega & r & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{\mathcal{Q}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -q \\ 0 & q & 0 \end{pmatrix}. \quad (5.60)$$

The eigenvalues of $\hat{\mathcal{M}}$ are:

$$v_1^{(0)} = 0, \quad v_2^{(0)} = r - i\omega, \quad v_3^{(0)} = r + i\omega. \quad (5.61)$$

The corresponding eigenvectors are the columns of the matrix:

$$V^{(0)} = \begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 1 & 0 & 0 \end{pmatrix}. \quad (5.62)$$

It is appropriate to treat $\hat{\mathcal{Q}}$ as a perturbation to $\hat{\mathcal{M}}$, given that $q^2 \ll \omega^2 + r^2$. Importantly, notice that both $\hat{\mathcal{M}}$ and $\hat{\mathcal{Q}}$ are non-Hermitian, so that the perturbation theory must be applied very carefully (Appendix E). The first-order corrections to the eigenvalues are

$$v_n^{(1)} = \langle n^{(0)} | \hat{\mathcal{Q}} | n^{(0)} \rangle, \quad (5.63)$$

where $|n^{(0)}\rangle$ with $n \in \{1, 2, 3\}$ is the n -th zero-order eigenvector (i.e. the n -th column of $V^{(0)}$). Here, $v_n^{(1)} = 0$ for all n . The first-order corrections to the eigenvectors are

$$|n^{(1)}\rangle = \sum_{m \neq n} \frac{-\mathcal{Q}_{mn}}{v_m^{(0)} - v_n^{(0)}} |m^{(0)}\rangle, \quad (5.64)$$

where $\mathcal{Q}_{mn} = \langle m | \hat{\mathcal{Q}} | n \rangle$. Thus, the perturbed eigenvectors are obtained as

$$V' = V^{(0)} + V^{(1)} = \begin{pmatrix} \frac{\omega\Omega^2}{q} & \frac{-i}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{r\Omega^2}{q} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 1 & \frac{\Omega^2(r+i\omega)}{\sqrt{2}q} & \frac{\Omega^2(r-i\omega)}{\sqrt{2}q} \end{pmatrix}, \quad (5.65)$$

where $\Omega^2 = q^2/(\omega^2 + r^2)$. The second-order corrections to the eigenvalues are

$$v_n^{(2)} = \sum_{m \neq n} \frac{-|\mathcal{Q}_{mn}|^2}{v_m^{(0)} - v_n^{(0)}}. \quad (5.66)$$

Then, the perturbed eigenvalues are

$$\begin{aligned} v_1' &= v_1^{(0)} + v_1^{(2)} = r\Omega^2, \\ v_2' &= v_2^{(0)} + v_2^{(2)} = (r - i\omega) - \frac{\Omega^2}{2}(r + i\omega), \\ v_2' &= v_2^{(0)} + v_2^{(2)} = (r + i\omega) - \frac{\Omega^2}{2}(r - i\omega). \end{aligned} \quad (5.67)$$

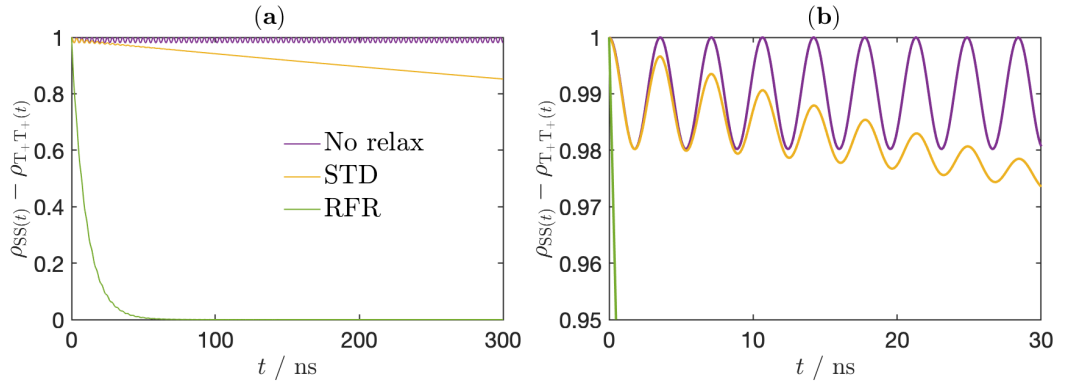


Figure 5.12: Time-dependent population difference between S and T_+ states. Purple, orange and green traces correspond to equations (5.56), (5.70) and (5.74), respectively. $q = 1$ mT, $\omega = 10$ mT and $r_{\text{STD}} = r_{\text{RFR}} = 5 \times 10^7 \text{ s}^{-1}$. Radical reactions are not included. (b) Expanded version of (a) showing time-dependence in the first 30 ns.

5.2. Origin of the time-dependence of $B_{1/2}$

Using equation (5.57),

$$p_{(t)} \approx V' e^{-\Lambda t} V'^{\dagger} p_{(0)}, \quad (5.68)$$

where Λ is the diagonal matrix with the three diagonal elements are v'_1 , v'_2 and v'_3 . Therefore,

$$p_{3(t)} = \rho_{SS(t)} - \rho_{T_+T_+(t)} = e^{-\Omega^2 r t} + \Omega^2 \cos\left(\left(1 + \frac{1}{2}\Omega^2\right)\omega t\right) e^{-(1-\frac{1}{2}\Omega^2)r t}. \quad (5.69)$$

Scaling equation (5.69) so that $p_{3(0)} = \rho_{SS(0)} - \rho_{T_+T_+(0)} = 1$ gives:

$$\rho_{SS(t)} - \rho_{T_+T_+(t)} \approx \frac{1}{1 + \Omega^2} e^{-\Omega^2 r t} + \frac{\Omega^2}{1 + \Omega^2} \cos(\omega t) e^{-r t}, \quad (5.70)$$

where we have used $\Omega^2 \ll 1$. The fast oscillation, characterized by $\cos(\omega t)$, between the S and T_+ states, with an extremely low amplitude $\Omega^2/(1 + \Omega^2)$, rapidly decays towards zero by the decoherence rate constant $r \gtrsim 10^7 \text{ s}^{-1}$ (much faster than the chemical reaction kinetics $\sim 10^6 \text{ s}^{-1}$ of radical pairs in Cry4a mutants). Thus, this oscillatory component is not expected to contribute to the time-dependent magnetic field effects. Surprisingly, shown in Figure 5.12, singlet-triplet dephasing further results in a long-term decay of the large population difference ($1/(1 + \Omega^2) \approx 1$). The decay rate constant depends on the applied magnetic field and the hyperfine interaction via $\Omega^2 = q^2/(\omega^2 + r^2)$. Taking $q = 1 \text{ mT}$, $\omega = 10 \text{ mT}$ and $r_{STD} = 5 \times 10^7 \text{ s}^{-1}$, the rate constant of such decay is $\Omega^2 r \approx 0.5 \times 10^6 \text{ s}^{-1}$ which is comparable to the reaction rate constants.

For comparison, the random fields relaxation is included in the S- T_+ model through relaxing the diagonal elements of the density matrix (the populations) towards 1/2 and the off-diagonal elements (the coherences) towards zero:

$$\begin{aligned} \frac{d\rho_{SS}}{dt} &= -r\rho_{SS} + r\rho_{T_+T_+}; & \frac{d\rho_{T_+T_+}}{dt} &= -r\rho_{T_+T_+} + r\rho_{SS}, \\ \frac{d\rho_{ST_+}}{dt} &= -r\rho_{ST_+}; & \frac{d\rho_{T_+S}}{dt} &= -r\rho_{T_+S}, \end{aligned} \quad (5.71)$$

where r denotes r_{RFR} , and the coherent dynamics induced by the spin Hamiltonian is omitted. Then, the relaxation superoperator is given,

$$\hat{W}_{\text{RFR}} = r \left(\hat{\mathbb{1}} - \hat{P}^{\text{ST}+} \otimes \hat{P}^{\text{T}+\text{S}} - \hat{P}^{\text{T}+\text{S}} \otimes \hat{P}^{\text{ST}+} \right) \quad (5.72)$$

where

$$\hat{P}^{\text{ST}+} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \hat{P}^{\text{T}+\text{S}} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (5.73)$$

Recalling the dynamical equation (5.59) for $p_{(t)}$ and applying the perturbation theory again, the time-dependent population difference is obtained as

$$p_{3(t)} = \rho_{\text{SS}(t)} - \rho_{\text{T}+\text{T}+(t)} \approx \frac{1}{1 + \Omega^2} e^{-2rt} + \frac{\Omega^2}{1 + \Omega^2} \cos(\omega t) e^{-rt}. \quad (5.74)$$

Same as STD, RFR damps the low-amplitude oscillation with the relaxation rate constant r . However, RFR also relaxes the population difference (with a rate constant $2r$) much faster than the chemical reactions (Figure 5.12). Thus, no time-dependent (until several microseconds) magnetic field effect could be brought about by RFR.

The effect of STD on the time-dependence of $B_{1/2}$ could be seen more closely with the symmetric reaction approximation (i.e. the “exponential model” in Ref [54]). Under an applied magnetic field stronger than the internal fields (i.e. $\Omega^2 \ll 1$ so as to drop the low-amplitude oscillatory term in equation (5.70)), remembering $\rho_{\text{SS}(t)} + \rho_{\text{T}+\text{T}+(t)} = 1$ gives

$$\rho_{\text{SS}(t, \omega)} = \frac{1}{2} + \frac{1}{2} e^{-\Omega^2 r t}. \quad (5.75)$$

Then, the time-dependent singlet (recombination) yield is obtained as

$$\begin{aligned} \Phi_{\text{r}(t, \omega)} &= k \int_0^t \rho_{\text{SS}(t', \omega)} e^{-kt'} dt' \\ &= \frac{1}{2} (1 - e^{-kt}) + \frac{k}{2(k + \Omega^2 r)} (1 - e^{-(\Omega^2 r + k)t}). \end{aligned} \quad (5.76)$$

5.2. Origin of the time-dependence of $B_{1/2}$

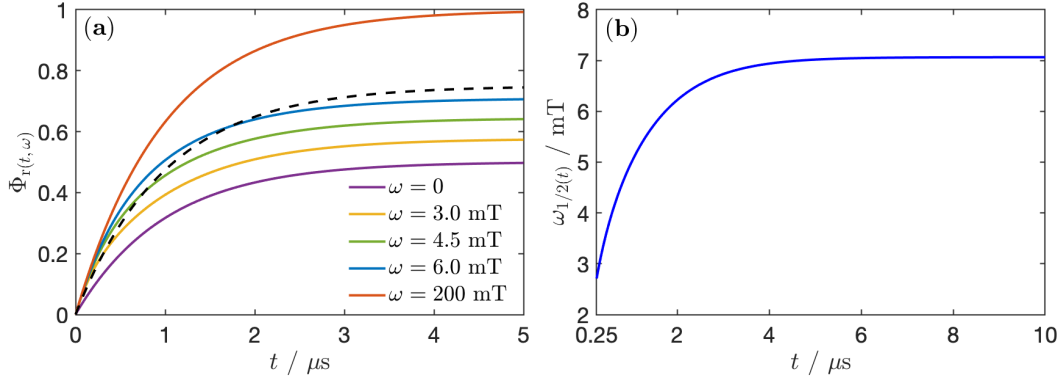


Figure 5.13: (a) Singlet yield as a function of time for five values of ω (0, 3, 4.5, 6 and 200 mT). The dashed black trace denotes $\Phi_{\text{r}(t, \omega_{1/2(t)})} = (\Phi_{\text{r}(t, 0)} + \Phi_{\text{r}(t, 200 \text{ mT})})/2$. (b) Time-dependent $\omega_{1/2(t)}$ with $0.25 < t < 10 \mu\text{s}$ obtained from equation (5.80).

When $\omega = \infty$ (note that in the calculation we use 200 mT to indicate ∞),

$$\Phi_{\text{r}(t, \infty)} = 1 - e^{-kt}. \quad (5.77)$$

Zero field makes S- T_+ interconversion identical to S- T_0 interconversion, so that $\Phi_{\text{r}(t, 0)}$ is obtained by recalling equation (5.54):

$$\Phi_{\text{r}(t, 0)} = \frac{1}{2}(1 - e^{-kt}). \quad (5.78)$$

According to equation (5.39), $\omega_{1/2}$ must satisfy:

$$\Phi_{\text{r}(t, \omega_{1/2})} = \frac{\Phi_{\text{r}(t, 0)} + \Phi_{\text{r}(t, \infty)}}{2}. \quad (5.79)$$

In Figure 5.13(a) where $q = 1 \text{ mT}$, $r_{\text{STD}} = 5 \times 10^7 \text{ s}^{-1}$ and $k = 10^6 \text{ s}^{-1}$, $\Phi_{\text{r}(t, \omega)}$ is shown for five values of ω (0, 3, 4.5, 6 and 200 mT) in $5 \mu\text{s}$. In order to obtain time-dependent $\omega_{1/2(t)}$, $(\Phi_{\text{r}(t, 0)} + \Phi_{\text{r}(t, 200 \text{ mT})})/2$ is illustrated by the black dashed line, which intersects the $\omega = 3.0, 4.5$ and 6.0 mT traces at $t = 0.31, 0.77$ and $1.74 \mu\text{s}$ respectively (i.e. $\omega_{1/2(0.31 \mu\text{s})} = 3.0 \text{ mT}$, $\omega_{1/2(0.77 \mu\text{s})} = 4.5 \text{ mT}$ and $\omega_{1/2(1.74 \mu\text{s})} = 6.0 \text{ mT}$). Combining equations (5.76 - 5.79) gives the algebraic relation which $\omega_{1/2(t)}$ obeys,

$$\frac{2k}{k + \Omega^2 r} (1 - e^{-(\Omega^2 r + k)t}) = 1 - e^{-kt}, \quad (5.80)$$

Solving equation (5.81) numerically (Figure 5.13(b)) shows that $\omega_{1/2(t)}$ increases from 2.71 mT at 0.25 μ s to 7.07 mT at 10.0 μ s. Remembering this is based on the two-level (S-T₊) model, a highly approximate model of the spin dynamics, it is notable that the obtained $\omega_{1/2(t)}$ can reasonably account for the time-dependent magnetic field effects (Figure 5.2, Table 5.2) measured in CRDS experiments.

5.3 Effect of STD on the directional sensitivity of the weak magnetic field

The repeatedly observed time-dependence of $B_{1/2}$ for the W369F mutants of avian Cry4a proteins [124, 125] can be satisfactorily explained by singlet-triplet dephasing. We have shown that STD with a rate constant $\sim 10^7$ s⁻¹ reasonably participates in the radical-pair spin dynamics due to the electron hopping between the two radical pairs, RP_B ([FAD^{•-} Trp_B^{•+}]) and RP_C ([FAD^{•-} Trp_C^{•+}]). For the wild-type Cry4a, which is supposed to account for the actual avian magnetore-

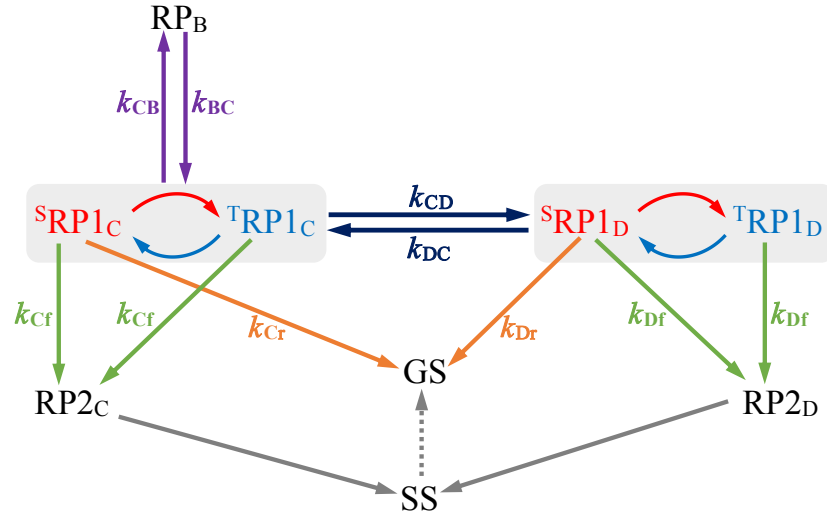


Figure 5.14: The radical-pair reaction scheme for the wild type Cry4a proteins developed from Ref [84]. $RP_B \rightleftharpoons RP_C$ and $RP_C \rightleftharpoons RP_D$ are included. Radical-pair recombination (to the ground state, GS) and protonation of the TrpH^{•+} radical (to RP2_C and RP2_D) are considered in RP1_C and RP1_D. The signalling state (SS) with a lifetime > 1 ms is supposed to be stabilized.

ception, the significant electron hopping between RP_C and RP_D ($[\text{FAD}^{\bullet-} \text{Trp}_\text{D}^{\bullet+}]$) is proposed [79, 84]. The rate constants of $\text{RP}_\text{C} \rightarrow \text{RP}_\text{D}$ and $\text{RP}_\text{D} \rightarrow \text{RP}_\text{C}$ are similar, both estimated to be of the order of 10^{10} s^{-1} [79]. Since the exchange interactions in RP_C and RP_D are very small (several microtesla) and the dipolar interactions for both radical pairs are not very different [79], $\text{RP}_\text{C} \rightleftharpoons \text{RP}_\text{D}$ is not likely to cause any appreciable decoherence process among the singlet and triplet states. However, a computational study [84] shows that $\text{RP}_\text{C} \rightleftharpoons \text{RP}_\text{D}$ indeed influences the weak magnetic field effect. Thus, the investigation of the weak magnetic field effect on the radical reactions including the interconversion among the three radical pairs is necessary.

5.3.1 Two-site hopping model

The spin-selective reactions in RP_C and RP_D are considered and RP_B is included only in the sense of the electron hopping between RP_B and RP_C (Figure 5.14). $\text{RP}_\text{B} \rightleftharpoons \text{RP}_\text{C}$ is equivalently represented by the singlet-triplet dephasing in the Liouvillian superoperator of RP_C . $\text{RP}_\text{C} \rightleftharpoons \text{RP}_\text{D}$ is realized by the two-site hopping model following Ref [84]. We have:

$$\begin{aligned} \frac{d\rho_\text{C}}{dt} &= -\hat{L}_\text{C}\rho_\text{C} - k_\text{CD}\rho_\text{C} + k_\text{DC}\rho_\text{D}, \\ \frac{d\rho_\text{D}}{dt} &= -\hat{L}_\text{D}\rho_\text{D} - k_\text{DC}\rho_\text{D} + k_\text{CD}\rho_\text{C}, \end{aligned} \quad (5.81)$$

where the Liouvillian superoperators are:

$$\hat{L}_\text{X} = i[\hat{H}_\text{X} \otimes \hat{\mathbb{1}} - \hat{\mathbb{1}} \otimes \hat{H}_\text{X}^\text{T}] + \frac{k_\text{Xr}}{2}(\hat{P}^\text{S} \otimes \hat{\mathbb{1}} + \hat{\mathbb{1}} \otimes \hat{P}^\text{S}) + k_\text{Xf}\hat{\mathbb{1}} + \hat{W}_\text{X} \quad (5.82)$$

in which $\text{X} = \text{C}, \text{D}$ and

$$\begin{aligned} \hat{W}_\text{C} &= r_\text{STD}(\hat{P}^\text{S} \otimes \hat{P}^\text{T} + \hat{P}^\text{T} \otimes \hat{P}^\text{S}) + r_\text{RFR}(\frac{3}{2}\hat{\mathbb{1}} - \sum_\text{J} \sum_k \hat{S}_{\text{J}k} \otimes \hat{S}_{\text{J}k}^\text{T}), \\ \hat{W}_\text{D} &= r_\text{RFR}(\frac{3}{2}\hat{\mathbb{1}} - \sum_\text{J} \sum_k \hat{S}_{\text{J}k} \otimes \hat{S}_{\text{J}k}^\text{T}), \end{aligned} \quad (5.83)$$

where $k = x, y, z$, and $J = 1$ denotes the $\text{FAD}^{\bullet-}$ radical and $J = 2$ denotes the $\text{TrpH}^{\bullet+}$ radical. Denoting σ_X as the row-wise flattened (vectorised) form of the matrix representation of ρ_X , we define σ as the double-length vector that contains the density matrix elements of both radical pairs:

$$\sigma = \begin{pmatrix} \sigma_C \\ \sigma_D \end{pmatrix}. \quad (5.84)$$

Therefore, equation (5.81) can be combined into a single matrix equation:

$$\frac{d\sigma}{dt} = -\hat{L}\sigma, \quad (5.85)$$

where $\hat{L}$, the combined Liouvillian, is the 2×2 block matrix:

$$\hat{L} = \begin{pmatrix} \hat{L}_C + k_{CD}\hat{\mathbb{1}} & -k_{DC}\hat{\mathbb{1}} \\ -k_{CD}\hat{\mathbb{1}} & \hat{L}_D + k_{DC}\hat{\mathbb{1}} \end{pmatrix} \quad (5.86)$$

At $t = 0$, the system is in the singlet RP1_C state, so that:

$$\sigma_{(0)} = \frac{1}{Z} \begin{pmatrix} \sigma_S \\ 0 \end{pmatrix} \quad (5.87)$$

where σ_S is the vectorised form of $\hat{P}^S$. Thus, the product yields of the forward reactions (the long-lived RP2) are obtained as:

$$\begin{aligned} \Phi_{Cf} &= k_{Cf} \int_0^\infty \text{Tr}\{\rho_{C(t)}\} dt = \frac{k_{Cf}}{Z} (\sigma_E \ 0) \hat{L}^{-1} \begin{pmatrix} \sigma_S \\ 0 \end{pmatrix}, \\ \Phi_{Df} &= k_{Df} \int_0^\infty \text{Tr}\{\rho_{D(t)}\} dt = \frac{k_{Df}}{Z} (0 \ \sigma_E) \hat{L}^{-1} \begin{pmatrix} \sigma_S \\ 0 \end{pmatrix}, \end{aligned} \quad (5.88)$$

where σ_E is the vectorised form of the identity operator. Then, the yield of the signalling state is:

$$\Phi_{SS} = \Phi_{Cf} + \Phi_{Df}. \quad (5.89)$$

As a measure of the directional sensitivity of the radical pair compass, we further define the anisotropy of the yield of the signalling state:

$$\Delta\Phi_{SS} = \max_{\theta, \phi}(\Phi_{SS}) - \min_{\theta, \phi}(\Phi_{SS}), \quad (5.90)$$

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where the maximum and minimum values of Φ_{SS} are determined by sampling a large number of geomagnetic field directions, (θ, ϕ) . $\Delta\Phi_{\text{SS}}$ is used to evaluate the directional sensitivity of the weak magnetic field.

5.3.2 Comparison of the effects of STD and RFR on $\Delta\Phi_{\text{SS}}$

N5 in $\text{FAD}^{\bullet-}$ (FN5) and N1 in $\text{TrpH}^{\bullet+}$ (WN1) are included in the calculation, and the hyperfine tensors are used following Ref [84]. The dipolar interactions in RP_{C} and RP_{D} are taken into account, and the dipolar tensors are used following Ref [84] (given in Table 5.4). The weak magnetic field $B = 50 \mu\text{T}$. The reaction rate constants (Figure 5.14) are $k_{\text{Cr}} = 9.3 \times 10^5 \text{ s}^{-1}$, $k_{\text{Cf}} = k_{\text{Df}} = 5.4 \times 10^5 \text{ s}^{-1}$, and $k_{\text{Dr}} = 3.4 \times 10^5 \text{ s}^{-1}$ (Table 5 and Ref [84]). The electron hopping rate constants [79] are $k_{\text{CD}} = 1.3 \times 10^{10} \text{ s}^{-1}$ and $k_{\text{DC}} = 1.5 \times 10^{10} \text{ s}^{-1}$. The effects of STD and RFR on $\Delta\Phi_{\text{SS}}$ are separately compared in Figure 5.15(a). Solely considering RFR (i.e. $r_{\text{STD}} = 0$), $\Delta\Phi_{\text{SS}}$ drops very fast when r_{RFR} becomes larger than 10^5 s^{-1} . The directional sensitivity would be destroyed by the RFR with $r_{\text{RFR}} \gtrsim 10^7 \text{ s}^{-1}$. By contrast, with $r_{\text{RFR}} = 0$, $\Delta\Phi_{\text{SS}}$ does not undergo a general decrease until r_{STD} becomes larger than 10^6 s^{-1} . With a STD with $r_{\text{STD}} \gtrsim 10^7 \text{ s}^{-1}$ (much faster than the chemical reactions), $\Delta\Phi_{\text{SS}}$ can even remain more than 50% of that without the inclusion of STD. Furthermore, $\Delta\Phi_{\text{SS}}$ does not continuously decline when

Radical Pair	D
F- W_{C}	$\begin{pmatrix} 0.0389 & -0.4325 & 0.1750 \\ -0.4325 & -0.2784 & 0.2506 \\ 0.1750 & 0.2506 & 0.2395 \end{pmatrix}$
F- W_{D}	$\begin{pmatrix} 0.0862 & -0.2196 & 0.0504 \\ -0.2196 & -0.2561 & 0.1031 \\ 0.0504 & 0.1031 & 0.1698 \end{pmatrix}$

Table 5.4: Dipolar tensors for F- $\text{W}_{\text{C/D}}$ calculated for *ClCry4a* in the FAD principal axis system, where F- $\text{W}_{\text{C/D}}$ stands for the radical pair $[\text{FAD}^{\bullet-} \text{Trp}_{\text{C/D}}\text{H}^{\bullet+}]$.

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k_{STD} rises beyond $\sim 10^7 \text{ s}^{-1}$. Conversely, $\Delta\Phi_{\text{SS}}$ increases when $10^7 \lesssim r_{\text{STD}} \lesssim 10^8 \text{ s}^{-1}$, a reasonable range for STD induced by $\text{RP}_{\text{B}} \rightleftharpoons \text{RP}_{\text{C}}$. Such enhancement of the directional sensitivity by STD, more generally the decoherence process among the electronic singlet and triplet states, is firstly reported in Ref [65]. This is

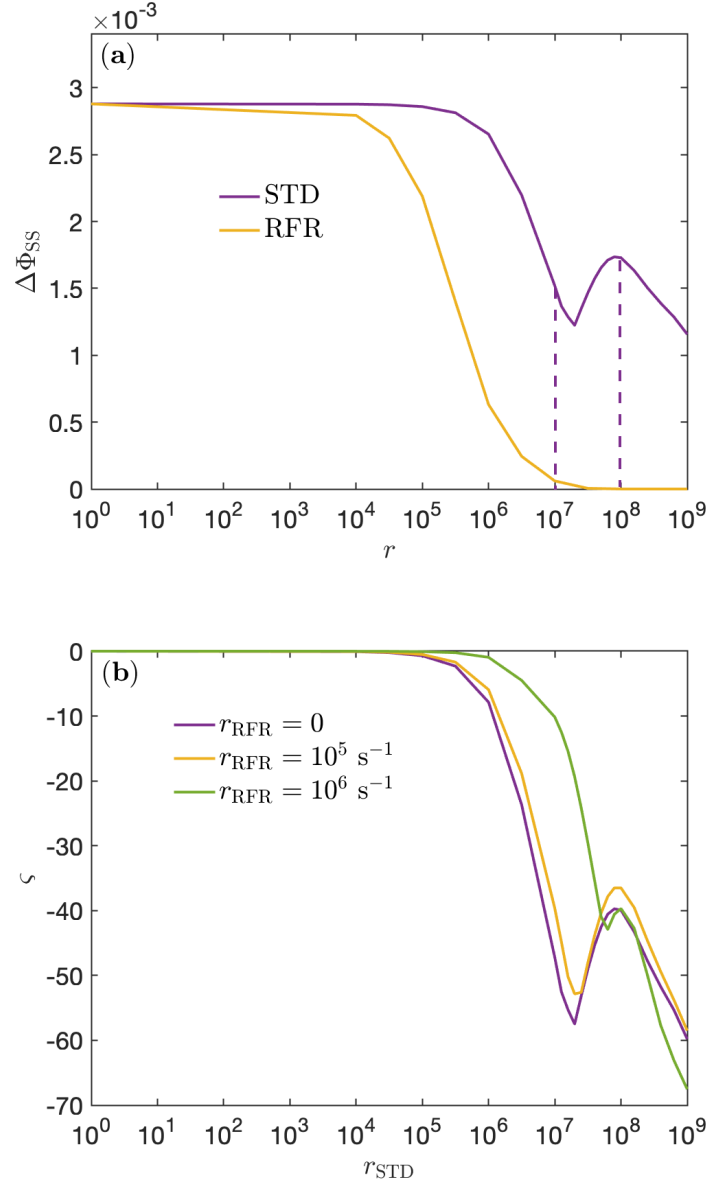


Figure 5.15: Two-site hopping model computation for the signalling state yields. (a) $\Delta\Phi_{\text{SS}}$ for solely including random fields relaxation or singlet-triplet dephasing. The relaxation rate constant varies in the range 10^0 - 10^9 s^{-1} . N5 is included in $\text{FAD}^{\bullet-}$ and N1 is included in $\text{TrpH}^{\bullet+}$. Hyperfine tensors and dipolar tensors in RP_{C} and RP_{D} are used following Ref [84]. (b) ζ defined in equation (5.91) with combining random fields relaxation and singlet-triplet dephasing.

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attributed to the decoherence induced long-term decay of the population difference between the singlet and triplet states, which can be regarded as a compensation for the singlet-triplet interconversion that is hindered by the energy gaps from the inter-radical interactions (e.g. the exchange and dipolar interactions). Such long-term decay is anisotropic with respect to the direction of the weak magnetic field: the field oriented along some direction can cause faster decay of the population difference than that along some other direction (Appendix F). Thus, the decoherence process, which conventionally thought to harm the magnetic field effect, can potentially enlarge the anisotropic weak field effect. It is notable that this enhancement can still be seen when STD only exists in RP_C and fast electron hopping occurs between RP_C and RP_D , both of which have dipolar interactions of several hundred microtesla.

Furthermore, the effect of STD combined with RFR is investigated. Signalling state yield is calculated with r_STD varying from 10^0 to 10^9 s^{-1} for three values of r_RFR (0 , 10^5 s^{-1} and 10^6 s^{-1}). ς is defined as

$$\varsigma = \frac{\Delta\Phi_{\text{SS}(r_\text{STD})} - \Delta\Phi_{\text{SS}(r_\text{STD}=0)}}{\Delta\Phi_{\text{SS}(r_\text{STD}=0)}}, \quad (5.91)$$

in order to quantify the effect of STD on the directional sensitivity with RFR included. In Figure 5.15(b), when $r_\text{RFR} < 10^6 \text{ s}^{-1}$, $\Delta\Phi_\text{SS}$ decreases less than 50% by the inclusion of STD with $r_\text{STD} < 10^8 \text{ s}^{-1}$. Moreover, ς rises at most 20% with $10^7 < r_\text{STD} < 10^8 \text{ s}^{-1}$, when r_RFR is at the order of 10^5 s^{-1} , meaning that the enhancement effect of STD can still be possible, if RFR is not so fast as 10^6 s^{-1} .

5.3.3 Estimation of r_RFR

Random fields relaxation (RFR) has been used to characterize the spin relaxation induced by the stochastic modulation of the intra-radical hyperfine interactions. The stochastically evolving variables are six fluctuating magnetic field components

$b_{Jk(t)}$ for $J = 1, 2$ and $k = x, y, z$. The local field fluctuations in RP1_C and RP1_D are assumed to have the same form. Then, the stochastic spin Hamiltonian is:

$$\hat{V}_{(t)} = \sum_j \sum_k -\gamma_e b_{Jk(t)} \hat{S}_{Jk}, \quad (5.92)$$

where $\gamma_e = -1.76 \times 10^{11} \text{ rad} \cdot \text{s}^{-1} \cdot \text{T}^{-1}$. Applying the Redfield approach in the extreme narrowing limit, we will obtain the relaxation superoperator:

$$\hat{R} = \int_0^\infty \langle \hat{V}_{(t)} \hat{V}_{(t-\tau)} \rangle d\tau = \sum_J r_J \left(\frac{3}{4} \hat{\mathbb{1}} - \sum_k \hat{S}_{Jk} \otimes \hat{S}_{Jk}^\dagger \right) \quad (5.93)$$

where $r_J = 2\gamma_e^2 \int \langle b_{Jk(t)} b_{Jk(t-\tau)} \rangle d\tau$. Note that $r_1 = r_2 = r_{\text{RFR}}$ will give rise to the representation of RFR in equation (5.83). However, in a realistic situation where the motion of the TrpH^{•+} is less restricted than that of the FAD^{•-} radical [63, 64], r_1 is not necessarily equal to r_2 . The librational motion of the radical is supposed to be isotropic, whereby $b_{Jk(t)}$ has the same distribution with different k . Note that the field fluctuations of different components of the two radicals are independent of each other. Thus, all the cross terms vanish (e.g. $\langle b_{1y(t)} b_{1z(t-\tau)} \rangle = \langle b_{1y(t)} \rangle \langle b_{1z(t-\tau)} \rangle = 0$). Choosing the field fluctuation to obey the Langevin equation [141], which is widely used to describe Brownian motions:

$$\frac{db_{Jk(\tau)}}{d\tau} = -\frac{1}{\tau_{cJ}} b_{Jk(\tau)} + \eta_{Jk(\tau)}, \quad (5.94)$$

where τ_{cJ} characterizes the correlation time-scale of the fluctuation in radical J , and $\eta_{Jk(\tau)}$ is the stochastic variable giving the effect of the background noise (i.e. $\langle \eta_{Jk(\tau)} \rangle = 0$). The formal solution of equation (1.30) is:

$$b_{Jk(\tau)} = e^{-\frac{\tau}{\tau_{cJ}}} b_{Jk(0)} + \int_0^\tau e^{-\frac{\tau-s}{\tau_{cJ}}} \eta_{Jk(s)} ds. \quad (5.95)$$

Then, $\langle b_{Jk(t)} b_{Jk(t-\tau)} \rangle$ is obtained by letting $t - \tau = 0$:

$$\langle b_{Jk(\tau)} b_{Jk(0)} \rangle = e^{-\frac{\tau}{\tau_{cJ}}} \langle b_{Jk(0)}^2 \rangle + \langle b_{Jk(0)} \int_0^\tau e^{-\frac{\tau-s}{\tau_{cJ}}} \eta_{Jk(s)} ds \rangle. \quad (5.96)$$

Note that the second term vanishes on averaging over the first-order noise. Thus, the RFR rate constant for radical j is obtained as $r_J = 2\tau_{cJ} \gamma_e^2 \langle b_{Jk(0)}^2 \rangle$. Directly

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measuring $\langle b_{Jk(0)}^2 \rangle$ is impossible, though $\langle b_{Jk(0)}^2 \rangle$ is known to be the variance in the case that $b_{Jk(0)}$ has a normal distribution.

Ref. [63] shows the molecular dynamics (MD) simulations for the FAD-based radical pair in *Arabidopsis thaliana* cryptochrome 1 (*AtCry1*), and the computational results with the spin relaxation induced by the modulation of the hyperfine interactions by the rotational motions. For a FAD-Z radical pair, the spin relaxation is mainly caused by the modulation of the anisotropic hyperfine interactions of the two nitrogens (i.e. N5 and N10) in the $\text{FAD}^{\bullet-}$ radical, which leads to a $\sim 11\%$ loss [63] of the singlet yield anisotropy Γ , defined as:

$$\Gamma = \frac{\Delta\Phi_S}{\langle\Phi_S\rangle} \times 100\% \quad (5.97)$$

where

$$\begin{aligned} \Delta\Phi_S &= \max_{\theta, \phi}(\Phi_S) - \min_{\theta, \phi}(\Phi_S), \\ \langle\Phi_S\rangle &= \frac{1}{4\pi} \iint \sin(\theta) \Phi_S d\theta d\phi. \end{aligned} \quad (5.98)$$

The anisotropy pattern, illustrated by the 3D polar plot in Ref. [63], is not changed by the relaxation. This is because the librations around the three (x , y and z) molecular axes are all $\sim 5^\circ$ in the $\text{FAD}^{\bullet-}$ radical, so that the relaxation is appropriately seen isotropic. Thus, we can apply RFR to the FAD-Z radical pair to find the proper relaxation rate constant that is equivalent to the exact spin relaxation from MD simulations in Ref [63]. In Figure 5.16, we see that RFR with $r_1 = 10^{5.25} \approx 1.8 \times 10^5 \text{ s}^{-1}$ gives rise to 11% loss of Γ . Note that RFR here describes the overall local internal magnetic field fluctuation for the electron in $\text{FAD}^{\bullet-}$, so that the distribution of $b_{1k(t)}$ can be estimated (t here can be any moment of time, e.g. $t = 0$). According to Ref. [63], the correlation time τ_{c1} is $\sim 1 \text{ ns}$. Therefore, $\langle b_{1k(0)}^2 \rangle = r_1 / (2\tau_{c1}\gamma_e^2) = 5.81 \times 10^{-9} \text{ T}^2$, and $b_{1k(t)}$ has a normal distribution with the mean $\mu = 0$ and the standard deviation $\sim 76 \text{ } \mu\text{T}$. The estimation of the RFR rate constant for $\text{TrpH}^{\bullet+}$, r_2 , could be difficult, since

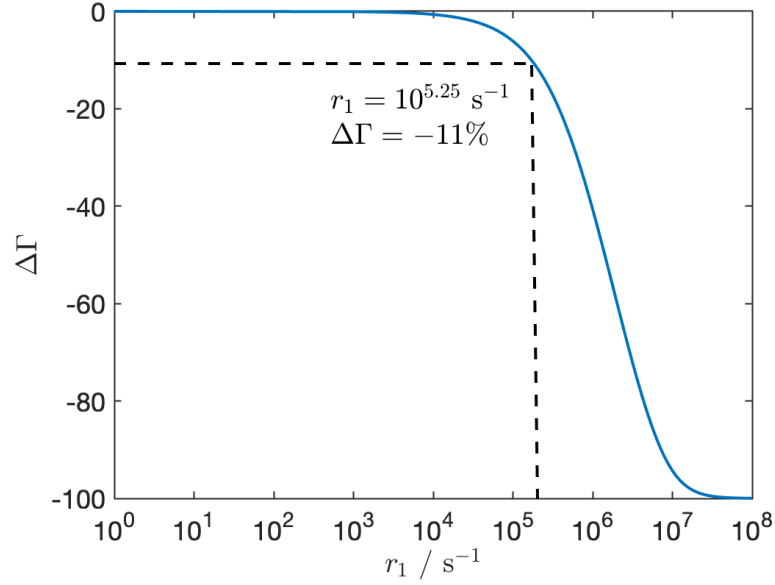


Figure 5.16: Change in Γ , defined in equation (5.97), of the FAD-Z radical pair brought about by random fields relaxation in the $\text{FAD}^{\bullet-}$ radical with r_1 in the range 10^0 - 10^8 s^{-1} . Here, $\text{Z}^{\bullet}$ is a radical with no hyperfine interactions and no contribution to the spin relaxation [63] ($r_2 = 0$).

there are more anisotropic hyperfine interactions in $\text{TrpH}^{\bullet+}$. An approximate prediction is that r_2 is still on the order of 10^5 s^{-1} , considering that the correlation time for the $\text{TrpH}^{\bullet+}$ radical is also $\sim 1 \text{ ns}$ and the librational motion is not far more vigorous (the librations around the molecular axes are all $\sim 11^\circ$) than that in the $\text{FAD}^{\bullet-}$ radical.

5.4 Conclusion

The time-dependent magnetic field effect on the radical pair reactions in W369F mutants of three avian (robin, chicken and pigeon) Cry4a proteins was repeatedly measured via cavity ring-down spectroscopy technique [124, 125]. In the pump-probe delay range less than $10 \mu\text{s}$, the values of $B_{1/2}$, which characterize the magnetic sensitivity of the radical pair, show a profound time dependence, rising from ~ 3 to $\sim 7 \text{ mT}$. This is consistent with the singlet-triplet dephasing mechanism with a rate constant $\sim 10^7 \text{ s}^{-1}$, which most likely originates in the electron hopping

between two components of the tryptophan-tetrad (i.e. Trp_B and Trp_C). Such fast decoherence process between the singlet and triplet states does not necessarily destroy the magnetic field effect - during a radical-pair lifetime around 1 μ s, MFE can still reach $\sim 20\%$ with the singlet-triplet dephasing 10 times faster than the chemical reactions. According to elaborate theoretical analysis, the time-dependence of $B_{1/2}$ is attributed to the dephasing induced long-term exponential approach to the spin equilibrium, which could take even longer time than the radical-pair lifetime. Furthermore, simulation on the wild type Cry4a, where the fast electron hopping between Trp_C and Trp_D is considered, shows that by contrast with the generic random fields relaxation caused by the stochastic modulation of the intra-radical magnetic fields, the singlet-triplet dephasing much faster than the chemical reactions in the FAD-Trp_C radical pair does not ruin the directional sensitivity of the weak magnetic field. Singlet-triplet dephasing with the reasonable rate constant ($\sim 10^7$ s⁻¹) preserves $\sim 50\%$ of the anisotropy of the signalling state yield, even under a random fields relaxation with a rate constant slower than 1 μ s⁻¹. Moreover, the enhancement of the directional sensitivity brought about by singlet-triplet dephasing can still be expected with $10^7 < r_{\text{STD}} < 10^8$ s⁻¹.

Chapter 6

Chiral-induced spin selectivity in radical-pair based magnetoreception

Due to conservation of electron spin angular momentum, the reactions of organic radicals are selective in the spin states of the unpaired electrons: pairs of radicals in electronic singlet (triplet) states are formed from and recombine to molecular singlet (triplet) states. The electronic singlet and triplet states are close in energy, so that the coherent interconversion between these spin states, induced by the intra-radical magnetic interactions (e.g. hyperfine interactions with nuclear spins), could be efficient during the lifetime of the radical pair. Application of external magnetic fields can remarkably modulate the spin dynamics and therefore the quantum yields of radical-pair reactions. Moreover, the reaction rates and yields are also sensitive to electron and nuclear spin polarization [142]. Studies of these phenomena have included radical pairs formed by photo-induced electron transfer reactions in proteins, in particular photosynthetic reaction centres [143] and the cryptochrome (Cry) flavoproteins thought to be responsible for the magnetic compass sense of migratory songbirds [97]. Dating back to the first experimental observations in the late 1960s and the development of the radical pair mechanism (RPM) [27, 50, 144–150], these and related effects constitute the field of spin chemistry [151].

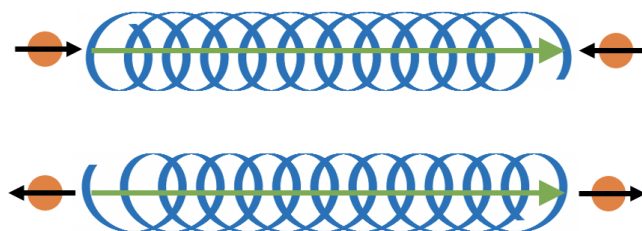


Figure 6.1: Scheme for a chiral (helical) molecule as the spin filter in electron transfer. The green arrows denote the electron motion. The black arrows denote the electron spins' polarization. The preferred electron spin polarization depends on the handedness of the molecule.

However, chiral-induced spin selectivity (CISS), discovered in the 1990s [152], seems to challenge the spin-conservation assumption that ignores the electronic spin evolution during the electron transfer process, the core basis for conventional RPM. It has become clear from the work of Naaman, Waldeck and colleagues that chiral molecules can act as spin filters that preferentially transmit electrons that have spins polarized either parallel or antiparallel to their direction of motion (Figure 6.1) [153–165]. Although the mechanism is not completely understood, most theoretical treatments appear to concur that CISS originates in the spin-orbit interaction of the spin with the linear momentum of electrons moving in the helical electrostatic potential of a chiral medium [154, 162, 166–172]. In a typical experiment, electrons are injected into a layer of chiral material, e.g. DNA, and emerge spin-polarized.

There have been speculations on its importance in biology [158, 163, 173–175], but it is not yet clear whether CISS should be expected to arise in electron transfer reactions of the type $D A \rightleftharpoons D^{\bullet+} A^{\bullet-}$ occurring, for example, in the chiral interior of a protein. Recent theoretical discussion [176, 177] suggests that spin-orbit couplings, with multi-step charge transport via $D^{\bullet+} A^{\bullet-}$ states with strong exchange interactions, could produce singlet-triplet coherence and generate CISS spin po-

larization. However, there is only one experimental report of CISS arising from an electron transfer reaction that creates a radical pair. Carmeli *et al* [174] have reported electron spin polarization in experiments on the photosynthetic reaction centre, photosystem I (PSI), a protein in which spin-correlated radical pairs are formed by light-induced charge separation between bound cofactors [178–181]. Using a spintronic detection device, with a monolayer of oriented PSI attached, Carmeli *et al* found strong spin selectivity throughout the photo-induced electron transfer pathway and established that the electrons were transferred with their spins aligned parallel to their momenta [174]. The only other overlap between CISS and the RPM of which we are aware is in the recombination of pairs of $\text{OH}^\bullet$ radicals but in that case the spin-correlation arises separately in two $\text{OH}^\bullet$ radicals created by conduction of electrons from OH^- ions to an electrode through an adsorbed layer of chiral molecules [164, 182–185].

Although there have been many hundreds of studies of radical pairs using electron paramagnetic resonance (EPR) spectroscopy [143, 178, 186, 187], a technique ideally suited for observing spin polarization, spin correlation and spin coherence, there seems to be no strong evidence for spin-selection effects that cannot be explained by the RPM. However, absence of evidence cannot be interpreted as evidence of absence. In this chapter, inspired by Carmeli *et al* [174], we start from the assumption that CISS can arise in radical pair reactions alongside the conventional RPM spin selectivity and attempt to answer the following questions. (1) How can CISS effects be included in the conventional modelling of radical pair spin dynamics? (2) How could CISS be detected by EPR and distinguished from RPM effects? (3) Could CISS be relevant to the cryptochrome hypothesis of the mechanism of the magnetic compass of migratory songbirds?

6.1 CISS in the formation and recombination of radical pairs

Consider the formation of a radical pair by the transfer of an electron from a closed shell donor to a photoexcited singlet acceptor:



Conventionally, such reactions conserve spin angular momentum and produce the radical pair predominantly in an electronic singlet state:

$$|S\rangle = \frac{1}{\sqrt{2}}(|\alpha_D\beta_A\rangle - |\beta_D\alpha_A\rangle), \quad (6.2)$$

where $|\alpha\rangle$ and $|\beta\rangle$ are the $m = \pm 1/2$ electron spin states. Here, the spin-orbit coupling is considered small for organic molecules. As is discussed in Chapter 2, subsequent recombination selects the spin states of the radical pair, including spin-selective back electron transfer to regenerate D and A in their (singlet) ground states:



and/or formation of the triplet state of one of the reactants, e.g.



Additionally there may be reactions that involve just one of the radicals (e.g. a change in protonation state), which are therefore not subject to spin-selection rules and occur at equal rates for singlet and triplet pairs, e.g.



Note that k_S , k_T and k_F are first-order rate constants. Such reactions are modelled by a Haberkorn master equation of the form:

$$\frac{d\rho(t)}{dt} = -i[\hat{H}, \rho(t)] - \frac{k_S}{2}\{\hat{P}^S, \rho(t)\} - \frac{k_T}{2}\{\hat{P}^T, \rho(t)\} - k_F\rho(t), \quad (6.6)$$

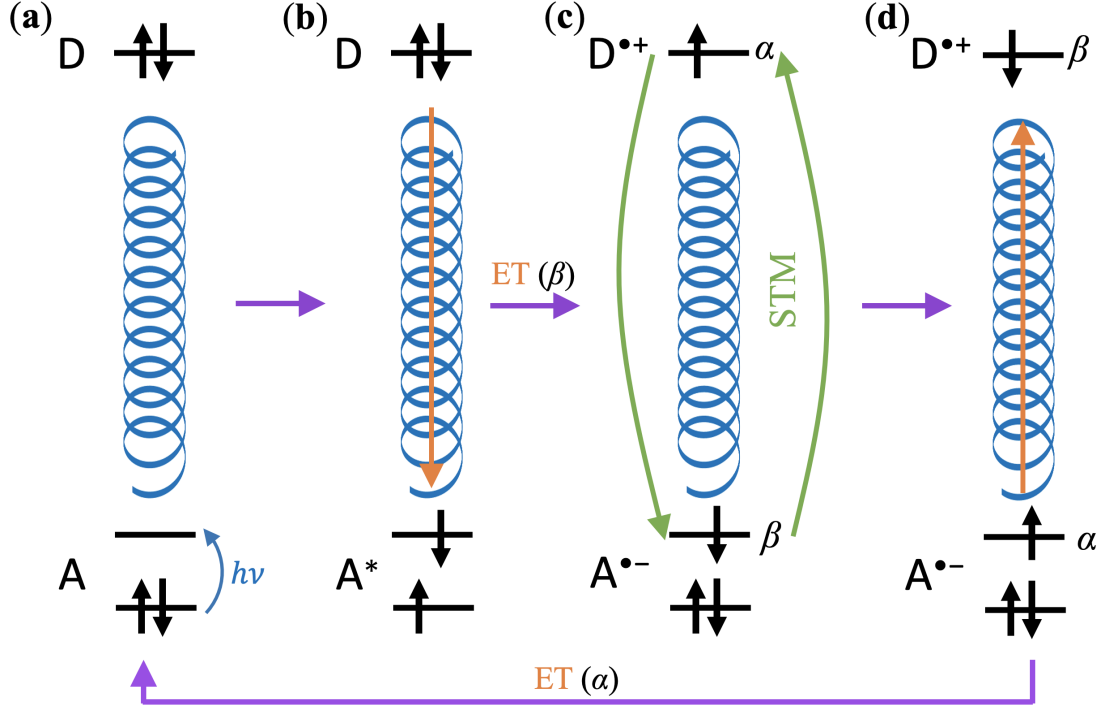


Figure 6.2: CISS effects in the formation and recombination of a radical pair. Up and down arrows denote α and β electron spins. (a) Photo-excitation of an acceptor molecule, A. (b) Electron transfer (ET), with spin β preferred by CISS, from a donor molecule, D, to A^* . (c) Singlet-triplet mixing in the radical pair $[D^{\bullet+} A^{\bullet-}]$, converting $|\alpha_D \beta_A\rangle$ to $|\beta_D \alpha_A\rangle$. (d) Back ET, with spin α preferred by CISS, from $A^{\bullet-}$ to $D^{\bullet+}$ to regenerate the ground state, A D. The spin quantization axis is taken to be the line of centres of the two radicals.

where $\hat{H}$ is the spin Hamiltonian for the radical pair,

$$\hat{H} = \boldsymbol{\omega} \cdot (\hat{\mathbf{S}}_D + \hat{\mathbf{S}}_A) + \sum_{i=D,A} \sum_k \hat{\mathbf{S}}_i \cdot \mathbf{A}_{ik} \cdot \hat{\mathbf{I}}_{ik} + \hat{\mathbf{S}}_D \cdot \mathbf{D} \cdot \hat{\mathbf{S}}_A - J \left(\frac{1}{2} \hat{\mathbf{1}} + 2 \hat{\mathbf{S}}_D \cdot \hat{\mathbf{S}}_A \right). \quad (6.7)$$

$\hat{\mathbf{S}}_D$ and $\hat{\mathbf{S}}_A$ are the electron spin operators of the two radicals and $\hat{\mathbf{I}}_{ik}$ is the spin operator of nucleus k in radical i . $\boldsymbol{\omega} = -\gamma_e B (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ is the external magnetic field vector (in angular frequency units) with magnitude $|\gamma_e|B$ and direction specified by angles θ and ϕ . $\mathbf{A}_{ik}$ is the hyperfine tensor that couples electron i with nucleus k . $\mathbf{D}$ and J are, respectively, the dipolar coupling tensor and the exchange interaction of the two electron spins.

6.1.1 Spin polarization caused by CISS

When the radical pair is formed by electron transfer in a chiral medium such as a protein, equation (6.6) needs to be modified to account for the CISS-type spin polarization effects. The limiting case of 100% CISS polarization suggests that only an electron with spin β can move from D to $^1A^*$ in reaction (6.1), leaving behind an electron with spin α in $D^{\bullet+}$ [163, 164]. Thus, the radical pair is initialized in the state $|\alpha_D\beta_A\rangle$ with the electron spins quantized along the direction of the electron transfer, i.e. the vector connecting the centres of D and A (Figure 6.2). Note that for the opposite chirality of the intervening medium, the initial state would be $|\beta_D\alpha_A\rangle$. In the general case, where the polarization is less than 100%, we propose that the initial state of the radical pair can be written $\hat{P}^I = |\psi_I\rangle\langle\psi_I|$ where

$$\begin{aligned} |\psi_I\rangle &= \cos\left(\frac{1}{2}\chi\right)|S\rangle + \sin\left(\frac{1}{2}\chi\right)|T_0\rangle \\ &= \frac{1}{\sqrt{2}}\left(\sin\left(\frac{1}{2}\chi\right) + \cos\left(\frac{1}{2}\chi\right)\right)|\alpha_D\beta_A\rangle + \frac{1}{\sqrt{2}}\left(\sin\left(\frac{1}{2}\chi\right) - \cos\left(\frac{1}{2}\chi\right)\right)|\beta_D\alpha_A\rangle, \end{aligned} \quad (6.8)$$

where $|T_0\rangle$ the $m = 0$ triplet state,

$$|T_0\rangle = \frac{1}{\sqrt{2}}(|\alpha_D\beta_A\rangle + |\beta_D\alpha_A\rangle). \quad (6.9)$$

Hence,

$$\begin{aligned} \hat{P}^I &= \frac{1}{2}(1 + \sin(\chi))|\alpha_D\beta_A\rangle\langle\alpha_D\beta_A| + \frac{1}{2}(1 - \sin(\chi))|\beta_D\alpha_A\rangle\langle\beta_D\alpha_A| \\ &\quad - \frac{1}{2}\cos(\chi)(|\alpha_D\beta_A\rangle\langle\beta_D\alpha_A| + |\beta_D\alpha_A\rangle\langle\alpha_D\beta_A|) \\ &= \frac{1}{4}\hat{1} - \hat{S}_{DZ}\hat{S}_{AZ} - (\hat{S}_{DX}\hat{S}_{AX} + \hat{S}_{DY}\hat{S}_{AY})\cos(\chi) + \frac{1}{2}(\hat{S}_{DZ} - \hat{S}_{AZ})\sin(\chi), \end{aligned} \quad (6.10)$$

in which $\hat{S}_{AQ}$ and $\hat{S}_{DQ}$ ($Q = X, Y, Z$) are components of the electron spin angular momentum operators of the two radicals. The Z -axis here is the CISS quantization axis. In equations (6.8) and (6.10), the angle χ determines the extent of the CISS polarization of the initial state, the limiting cases being $\chi = 0$,

$\hat{P}^I = |S\rangle\langle S|$ (pure singlet, no CISS) and $\chi = \pi/2$, $\hat{P}^I = |\alpha_D\beta_A\rangle\langle\alpha_D\beta_A|$ (100% CISS, no RPM). The four operator terms in the final line of equation (6.10) are as follows: the identity operator, two-spin order, zero quantum coherence (ZQC), and single-spin polarizations, all defined with respect to the CISS Z -axis. It is clear that a CISS contribution to the initial state modifies the amplitude of the ZQC and introduces equal and opposite spin polarization in the two radicals.

The CISS effect couples the linear momentum of an electron to its spin angular momentum such that electron transport is more efficient when they are either parallel or antiparallel, depending on the chirality of the medium [154]. This correlation implies that if only an electron with spin β can move from D to $^1A^*$ then only an electron with spin α can move in the opposite direction when the electron returns from $A^{\bullet-}$ to $D^{\bullet+}$ (Figure 6.2). We therefore propose that the corresponding projection operator for back electron transfer should be $\hat{P}^R = |\psi_R\rangle\langle\psi_R|$ where

$$\begin{aligned} |\psi_R\rangle &= \cos\left(\frac{1}{2}\chi\right)|S\rangle - \sin\left(\frac{1}{2}\chi\right)|T_0\rangle \\ &= -\frac{1}{\sqrt{2}}\left(\sin\left(\frac{1}{2}\chi\right) - \cos\left(\frac{1}{2}\chi\right)\right)|\alpha_D\beta_A\rangle - \frac{1}{\sqrt{2}}\left(\sin\left(\frac{1}{2}\chi\right) + \cos\left(\frac{1}{2}\chi\right)\right)|\beta_D\alpha_A\rangle, \end{aligned} \quad (6.11)$$

and

$$\hat{P}^R = \frac{1}{4}\hat{1} - \hat{S}_{DZ}\hat{S}_{AZ} - (\hat{S}_{DX}\hat{S}_{AX} + \hat{S}_{DY}\hat{S}_{AY})\cos(\chi) - \frac{1}{2}(\hat{S}_{DZ} - \hat{S}_{AZ})\sin(\chi). \quad (6.12)$$

The only difference between $\hat{P}^I$ and $\hat{P}^R$ is the sign of the spin-polarization term, $(\hat{S}_{DZ} - \hat{S}_{AZ})$. χ plays the same role here as in equations (6.8) and (6.10), with limiting cases $\chi = 0$, $\hat{P}^R = |S\rangle\langle S|$ (pure singlet, no CISS) and $\chi = \pi/2$, $\hat{P}^R = |\beta_D\alpha_A\rangle\langle\beta_D\alpha_A|$ (100% CISS, no RPM). If $|\beta_D\alpha_A\rangle$ is favoured over $|\alpha_D\beta_A\rangle$ in the forward electron transfer, and vice-versa in the recombination step, χ will be in the range $[0, -\pi/2]$.

Assuming the rate of the triplet reaction in equation (6.4) is negligible (as is the case in cryptochromes [53]), the master equation for the density operator with CISS effects included becomes

$$\frac{d\rho(t)}{dt} = -i[\hat{H}, \rho(t)] - \frac{k_R}{2}\{\hat{P}^R, \rho(t)\} - k_F\rho(t), \quad (6.13)$$

where k_R is the rate constant for back electron transfer, $[D^{\bullet+} A^{\bullet-}] \rightarrow D + A$, and the initial state of the radical pair is $\rho_{(0)} = \hat{P}^I/Z$ with Z the nuclear spin dimension. We propose equations (6.10) and (6.12) here in the same spirit as the Haberkorn approach [87] in an attempt to merge Carmeli's observations of electron spin polarization in photosynthetic reaction centres [174] with the conventional RPM. Other formulations are possible. For example, the singlet and triplet parts of $|\psi_I\rangle$ and $|\psi_R\rangle$ could have different phases, in the sense of the potential additional singlet-triplet coherence produced by the spin-orbit coupling in the electron transfer through a chiral medium [176], and $\hat{P}^I$ and $\hat{P}^R$ could be mixed states instead of pure states. An advantage of the forms we have chosen is that they involve the minimum number of parameters.

The formation of a radical pair in a spin-polarized $|\alpha_D\beta_A\rangle$ or $|\beta_D\alpha_A\rangle$ state from singlet state precursors is reminiscent of the ALTADENA (Adiabatic Longitudinal Transport After Dissociation Engenders Net Alignment) effect in which molecules, formed by reaction with para-hydrogen (p-H₂, a nuclear singlet state, $1/\sqrt{2}(|\alpha_1\beta_2\rangle - |\beta_1\alpha_2\rangle)$) in a weak magnetic field, are transferred adiabatically into the strong magnetic field of an NMR spectrometer [188–190]. Transport from a situation in which the nuclear spin-spin interaction dominates the nuclear Zeeman interaction to one in which the Zeeman interactions are much larger than the spin-spin coupling results in the population of only one of the four high-field nuclear spin states, $|\alpha_1\beta_2\rangle$ or $|\beta_1\alpha_2\rangle$. At least phenomenologically, it appears that the CISS effect can be thought of in the same way. One starts with

the electronic singlet state of the photo-excited precursor in which the electron exchange interaction is very large, and ends in a radical pair state that has very weak electron-electron coupling. The difference from ALTADENA, is that with CISS there is no obvious parallel to the strong NMR field. However, the origin of CISS is often described in terms of an effective magnetic field, arising from the motion of the electrons in a helical electrostatic potential, which leads via spin-orbit coupling to the spin polarization.

6.1.2 EPR detection of the CISS effect

The radical-pair spin state affected by CISS could manifest in the EPR spectra. Consider the simple case of a weakly coupled pair of electrons, with different g -values, an isotropic exchange interaction, and no dipolar or hyperfine interactions. Then, the spin Hamiltonian for the radical pair is

$$\hat{H} = \omega_D \hat{S}_{Dz} + \omega_A \hat{S}_{Az} - J \left(\frac{1}{2} \hat{1} + 2 \hat{\mathbf{S}}_D \cdot \hat{\mathbf{S}}_A \right), \quad (6.14)$$

where $\omega_{D(A)} = g_{D(A)} \mu_B \hbar^{-1} B_0$ in which $g_{D(A)}$ denotes the g -factors of the electrons in the two radicals. In the weak coupling limit, i.e. $|\omega_A - \omega_D|/2 \gg |J|$, the four eigenstates and their eigenvalues are [191]:

$$\begin{aligned} |1\rangle &= |\alpha_D \alpha_A\rangle & \omega_1 &= \frac{1}{2}(\omega_D + \omega_A) - J, \\ |2\rangle &= |\beta_D \alpha_A\rangle & \omega_2 &= \frac{1}{2}(\omega_A - \omega_D), \\ |3\rangle &= |\alpha_D \beta_A\rangle & \omega_3 &= \frac{1}{2}(\omega_D - \omega_A), \\ |4\rangle &= |\beta_D \beta_A\rangle & \omega_4 &= -\frac{1}{2}(\omega_D + \omega_A) - J. \end{aligned} \quad (6.15)$$

We assume that $J < 0$ and $\omega_A > \omega_D$. At thermal equilibrium, the populations of the four eigenstates are $p_1 < p_2 = p_3 < p_4$ characterized by $-(\hat{S}_{Dz} + \hat{S}_{Az})$, so that the EPR spectrum would comprise four equally (absorption) intense lines (Figure 6.3(a)). If the same radical pair were created by electron transfer, with the magnetic field of the EPR spectrometer (z) aligned parallel to the CISS

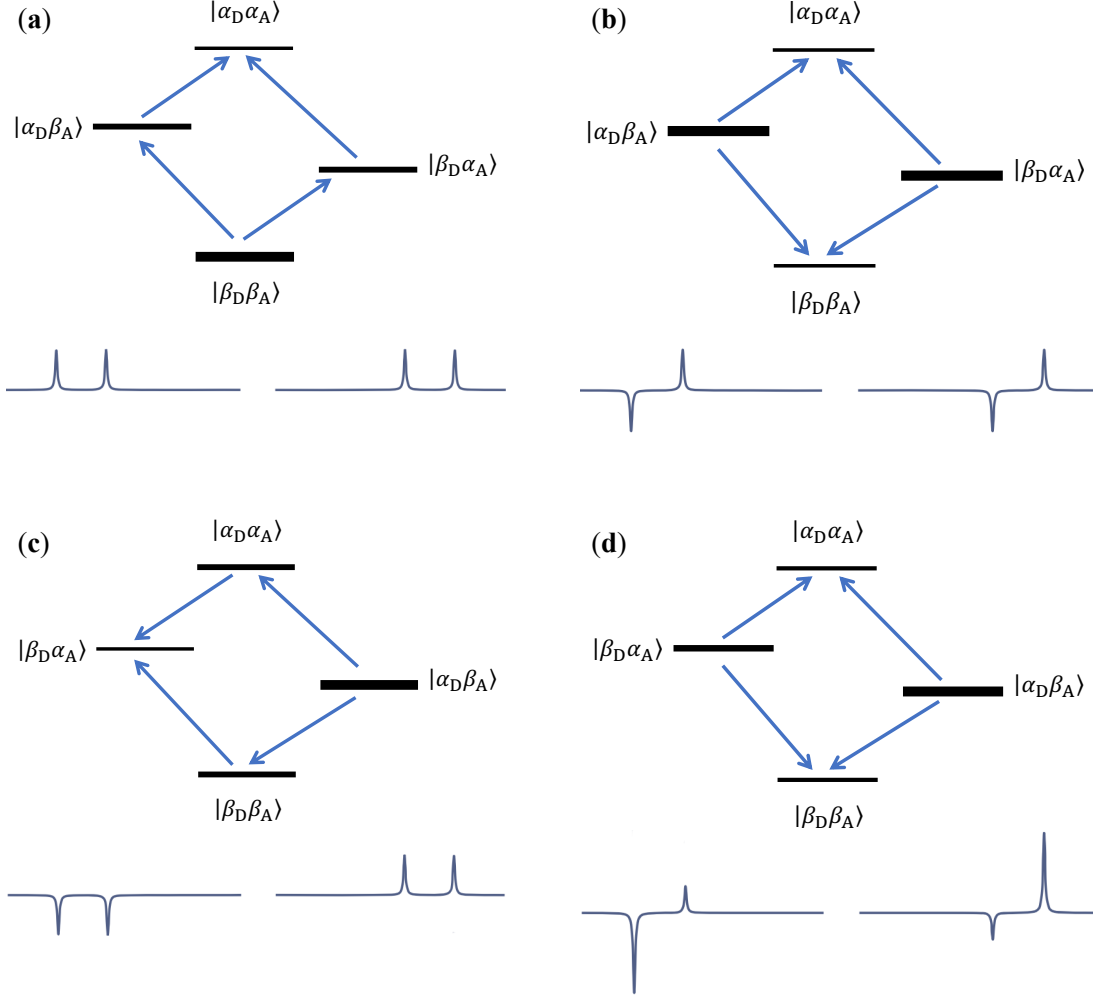


Figure 6.3: Schematic transitions and EPR spectra of a pair of weakly coupled electron spins in various initial spin states: (a) $-(\hat{S}_{Dz} + \hat{S}_{Az})$; (b) $-\hat{S}_{Dz}\hat{S}_{Az}$; (c) $\hat{S}_{Dz} - \hat{S}_{Az}$; (d) $-\hat{S}_{Dz}\hat{S}_{Az} + \frac{1}{2}(\hat{S}_{Dz} - \hat{S}_{Az}) \sin(\chi)$.

quantization axis (Z), the initial spin state, $\rho_{(0)} = \hat{P}^I/Z$, would be given by equation (6.10) with X, Y, Z replaced by x, y, z , respectively:

$$\hat{P}^I = \frac{1}{4}\hat{1} - \hat{S}_{Dz}\hat{S}_{Az} - (\hat{S}_{Dx}\hat{S}_{Ax} + \hat{S}_{Dy}\hat{S}_{Ay}) \cos(\chi) + \frac{1}{2}(\hat{S}_{Dz} - \hat{S}_{Az}) \sin(\chi). \quad (6.16)$$

When there is no CISS contribution ($\chi = 0$), $\rho_{(0)}$ comprises correlated two-spin polarization, $\hat{S}_{Dz}\hat{S}_{Az}$, and ZQC, $(\hat{S}_{Dx}\hat{S}_{Ax} + \hat{S}_{Dy}\hat{S}_{Ay})$ [192, 193]. In a continuous wave, time-resolved EPR experiment, in which the magnetic field is swept in the presence of a constant microwave field, the oscillatory ZQC term would average, leaving only the two-spin order [191]. The latter gives rise to the antiphase

doublets, $-\hat{S}_{Dz}\hat{S}_{Az}$, that are characteristic of spin-correlated radical pairs, so that $p_1 = p_4 < p_2 = p_3$, leading to transitions from $|2\rangle$ and $|3\rangle$ to $|1\rangle$ (absorption) and $|4\rangle$ (emission) (Figure 6.3(b)) [191, 194–197]. In the same experiment, the final term in equation (6.16), $\hat{S}_{Dz} - \hat{S}_{Az}$, which would most clearly reveal a CISS effect giving $p_2 < p_1 = p_4 < p_3$, corresponds to the spectrum in Figure 6.3(c) in which the doublet signals of the two radicals are equally and oppositely polarized. In general, when $0 \leq \chi \leq \pi/2$ so that $p_1 = p_4 \leq p_2 \leq p_3$, the EPR spectrum (Figure 6.3(d)) would be a linear combination of Figure 6.3(b) and (c) with the inner pair of lines in the four-line spectrum stronger or weaker than the outer pair.

Now contrast this with the situation in which the spectrometer field along the z -axis is parallel to the molecular X -axis, so that the CISS quantization Z -axis is parallel to the x -axis. The initial state is now given by:

$$\hat{P}^I = \frac{1}{4}\hat{1} - \hat{S}_{Dx}\hat{S}_{Ax} - (\hat{S}_{Dy}\hat{S}_{Ay} + \hat{S}_{Dz}\hat{S}_{Az})\cos(\chi) + \frac{1}{2}(\hat{S}_{Dx} - \hat{S}_{Ay})\sin(\chi). \quad (6.17)$$

The coherences, i.e. x and y operator terms in equation (6.17), are assumed to be averaged out in a continuous wave, time-resolved experiment. Then, we are left with

$$\hat{P}^I = \frac{1}{4}\hat{1} - \hat{S}_{Dz}\hat{S}_{Az}\cos(\chi), \quad (6.18)$$

so that the spectrum would resemble Figure 6.3(b) rather than Figure 6.3(d). Thus, one could expect a clear difference in the spectra when the magnetic field is parallel and perpendicular to the CISS axis. The schematic spectra in Figure 6.3 are for an ensemble of idealised, aligned radical pairs. In reality, one would need to consider also g -anisotropy, dipolar and hyperfine interactions [191, 194, 197]. Nevertheless, it might be possible to identify the contribution from the $\hat{S}_{Dz} - \hat{S}_{Az}$ term which would be diagnostic of a CISS component in the spin selectivity.

For a randomly oriented ensemble of radical pairs one would have to average over all directions of the magnetic field with respect to the CISS quantization axis. Rotating $\hat{P}^I$ in equation (6.10) from the molecular frame (X, Y, Z) to the laboratory frame (x, y, z) gives:

$$\begin{aligned} \rho_{(0)} \propto e^{-i\hat{S}_{DAy}\theta_C} \hat{P}^I e^{i\hat{S}_{DAy}\theta_C} &= \frac{1}{4}\hat{1} - \hat{S}_{Dz}\hat{S}_{Az}(\cos^2(\theta_C) + \sin^2(\theta_C)\cos(\chi)) \\ &+ \frac{1}{2}\cos(\theta_C)\sin(\chi)(\hat{S}_{Dz} - \hat{S}_{Az}) + \dots \end{aligned} \quad (6.19)$$

where θ_C is the angle between the magnetic field and the CISS axis, $\hat{S}_{DAq} = \hat{S}_{Dq} + \hat{S}_{Aq}$, and only the non-oscillating polarization terms, involving exclusively z -operators, have been retained. Spherical averaging causes the $(\hat{S}_{Dz} - \hat{S}_{Az})$ term to vanish, leaving the average initial state:

$$\langle \rho_{(0)} \rangle \propto \frac{1}{4}\hat{1} - \hat{S}_{Dz}\hat{S}_{Az}\left(\frac{1}{3} + \frac{2}{3}\cos(\chi)\right). \quad (6.20)$$

The spectrum would therefore comprise antiphase doublets (Figure 6.4(b)), as expected in the absence of CISS. Any CISS effects would therefore be difficult to distinguish from the conventional RPM polarization. Finally, we consider the electron spin echo envelope modulation (ESEEM) experiment which has been used extensively to determine the distance between radicals in radical pairs via the echo modulation arising from the electron dipolar coupling [192, 198–200]. Applying the pulse sequence $(45^\circ) - \tau - (180^\circ) - \text{echo}$ [192, 201] to $\rho_{(0)}$ in equation (6.19) gives the expected out-of-phase component from the $\hat{S}_{Dz}\hat{S}_{Az}$ term,

$$-\frac{1}{2}\sin(2J\tau)(\hat{S}_{Dx} + \hat{S}_{Ax})(\cos^2(\theta_C) + \sin^2(\theta_C)\cos(\chi)), \quad (6.21)$$

as well as a signal in the in-phase channel originating in the $(\hat{S}_{Dz} - \hat{S}_{Az})$ term,

$$\frac{1}{2\sqrt{2}}\cos(2J\tau)(\hat{S}_{Dy} - \hat{S}_{Ay})\cos(\theta_C)\sin(\chi). \quad (6.22)$$

As before, the latter should be observable for an oriented sample but would average to zero for a randomly oriented collection of radical pairs.

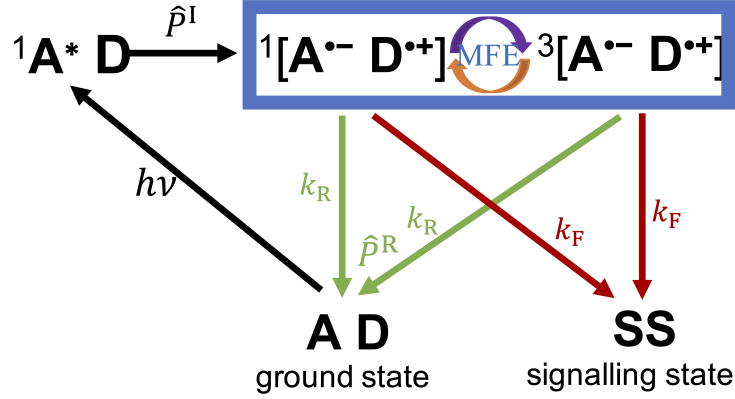


Figure 6.4: Scheme for the radical pair reactions including CISS.

6.2 Magnetic field effects

We use the reaction scheme in Figure 6.4 to assess the effects of including CISS in the radical pair model of magnetoreception in migratory birds. In cryptochrome, the donor and acceptor radicals are $\text{TrpH}^{\bullet+}$ and $\text{FAD}^{\bullet-}$, respectively, formed by intra-protein electron transfer from a tryptophan residue (TrpH) to the photo-excited singlet state of the non-covalently bound chromophore, flavin adenine dinucleotide (FAD) [53]. This reaction is spin-selective ($\rho_{(0)} = \hat{P}^I$) and is assumed to be much faster than subsequent processes. The radical pair undergoes coherent spin dynamics as a result of the Zeeman, hyperfine, dipolar and exchange interactions and either reverts to the ground state with rate constant k_R and spin-selectivity given by $\hat{P}^R$, or reacts non-spin-selectively with rate constant k_F to give a signalling state of the protein. The latter is thought to occur via deprotonation and subsequent reduction of the $\text{TrpH}^{\bullet+}$ radical, and protonation of the $\text{FAD}^{\bullet-}$ radical, to give a state of the cryptochrome with altered binding affinity to a signalling partner [202]. The ultimate yield of the signalling state once all radical pairs have reacted is

$$\Phi_F = k_F \int_0^\infty \text{Tr}\{\rho_{(t)}\} dt, \quad (6.23)$$

Time evolution of $\rho_{(t)}$ is driven by equation (6.13). Φ_F depends on the direction of the external magnetic field through the anisotropy of the hyperfine and dipolar interactions (and CISS when $\chi \neq 0$) and is the source of the directional information from which the bird is assumed to derive a compass bearing. In what follows, we present this information as $\Phi_S = 1 - \Phi_F$, the yield of the recombination reaction. Φ_R was calculated, in Hilbert space using the method in Section 2.4.2, Chapter 2, for a range of magnetic field directions (θ, ϕ) (equation (6.7)) to obtain the following measure of the anisotropy of the reaction yield:

$$\Delta\Phi_R = -\Delta\Phi_F = \max_{\theta, \phi} \{\Phi_R\} - \min_{\theta, \phi} \{\Phi_R\}. \quad (6.24)$$

6.2.1 Toy radical pair

To get a clear initial impression of the changes that can be expected when CISS effects are included, we start with a radical pair with the simplest possible internal magnetic interactions. One radical contains a single spin-1/2 nucleus with an axial hyperfine interaction and principal components $a_{xx} = a_{yy} = 0$, $a_{zz} = 1.5$ mT. The other radical has no nuclear spins. The electron–electron dipolar interaction, $D = -0.4$ mT, corresponds to the ~ 1.9 nm separation of $\text{FAD}^{\bullet-}$ and $\text{Trp}_C\text{H}^{\bullet+}$ [134] where Trp_CH is the third of the four tryptophan residues that make up the electron transfer chain in avian Cry4 [203–207]. The CISS quantization axis is taken to be parallel to the dipolar axis (the line of centres of the two radicals) which makes an angle of 45° with the hyperfine z -axis. The exchange interaction of the two electrons in $[\text{FAD}^{\bullet-} \text{Trp}_C\text{H}^{\bullet+}]$ is much smaller than D [79, 205], and we have taken it to be zero here.

Figure 6.5 shows the time-dependent probability of the recombination-selected spin state, $\text{Tr}\{\hat{P}^R \rho_{(t)}\}$ in the absence of any external magnetic field, for pure RPM ($\chi = 0$) and pure CISS ($\chi = \pi/2$) without taking chemical reactions into account.

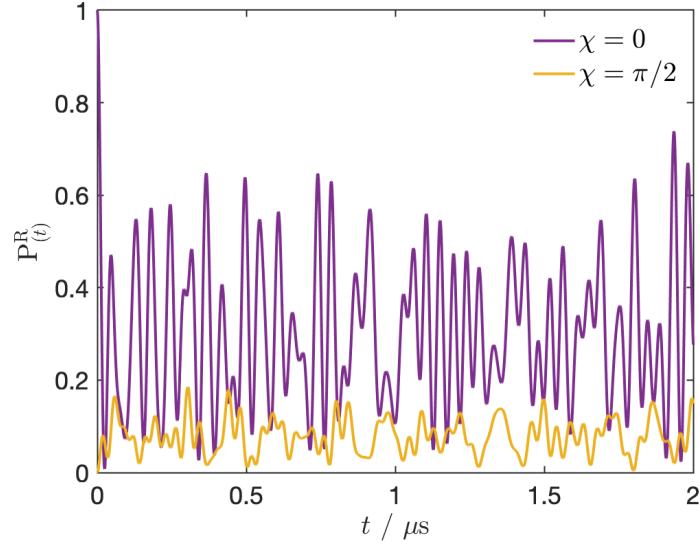


Figure 6.5: Time-dependent probability of the recombination-selected spin state, $\text{Tr}\{\hat{P}^R \rho(t)\}$ of the toy radical pair for RPM ($\chi = 0$) and CISS ($\chi = \pi/2$). No external magnetic field is considered.

It is clear to see that pure RPM produces much greater fraction for $\text{Tr}\{\hat{P}^R \rho(t)\}$ than pure CISS. Hence, we speculate that with a strong CISS effect, k_R must be much larger than k_F to make an effective competition between the channels of recombination and forward spin-selective reactions - a significant condition for a weak external magnetic field to have notable influence on the reaction yield. The time-dependent yields of the recombination and forward reactions, including the chemical reactions in Figure 6.4, are illustrated in Figure 6.6. Taking $k_F = 10^6 \text{ s}^{-1}$, to cause comparable production rates for the recombination and forward reaction yields, k_R only needs to be $\sim 3 \times 10^6 \text{ s}^{-1}$ in pure RPM (Figure 6.6(a)), whereas in pure CISS, the back electron transfer has to be ~ 30 times faster than the forward reactions, i.e. $k_R \simeq 3 \times 10^7 \text{ s}^{-1}$ (Figure 6.6(b)).

Applying a weak external magnetic field with the strength $50 \mu\text{T}$, approximately the mean geomagnetic field, we calculate reaction yield anisotropy ($\Delta\Phi_R$, equation (6.24)) as a function of k_R and k_F for six values of the CISS efficiency parameter,

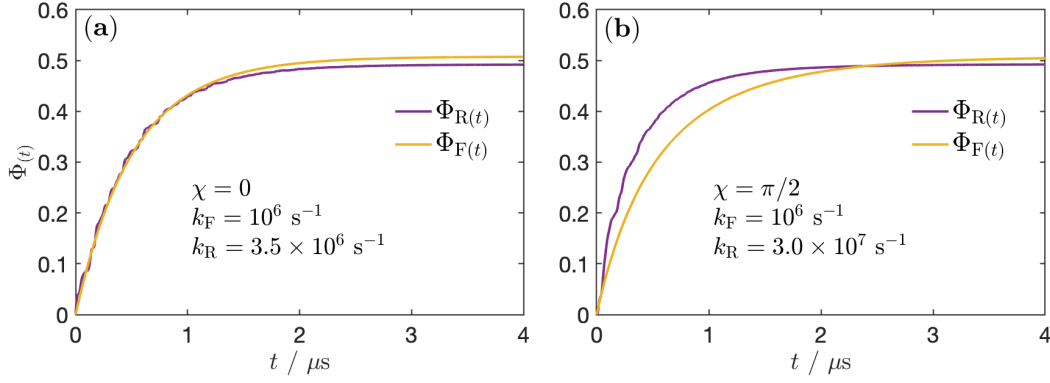


Figure 6.6: Time-dependent reaction yields of the toy radical pair for (a) $\chi = 0$, $k_F = 10^6 \text{ s}^{-1}$ and $k_R = 3.5 \times 10^6 \text{ s}^{-1}$ and for (b) $\chi = \pi/2$, $k_F = 10^6 \text{ s}^{-1}$ and $k_R = 3.0 \times 10^7 \text{ s}^{-1}$.

χ (Figure 6.7). Without CISS ($\chi = 0$), the maximum anisotropy (~ 0.007) is small and occurs when $k_R \approx k_F \leq 10^7 \text{ s}^{-1}$ [208]. As the contribution of CISS polarization in the formation and recombination steps is increased, the maximum value of $\Delta\Phi_R$ increases (by a factor of ~ 20 when $\chi = \pi/2$, pure CISS) and now occurs when $k_R \gg k_F$. Figures 6.8(a) and (b) show the shape (the 3D polar plots introduced in Chapter 4) of the anisotropy of the reaction yield, Φ_R , for two sets of rate constants chosen to be close to the conditions that maximise $\Delta\Phi_R$

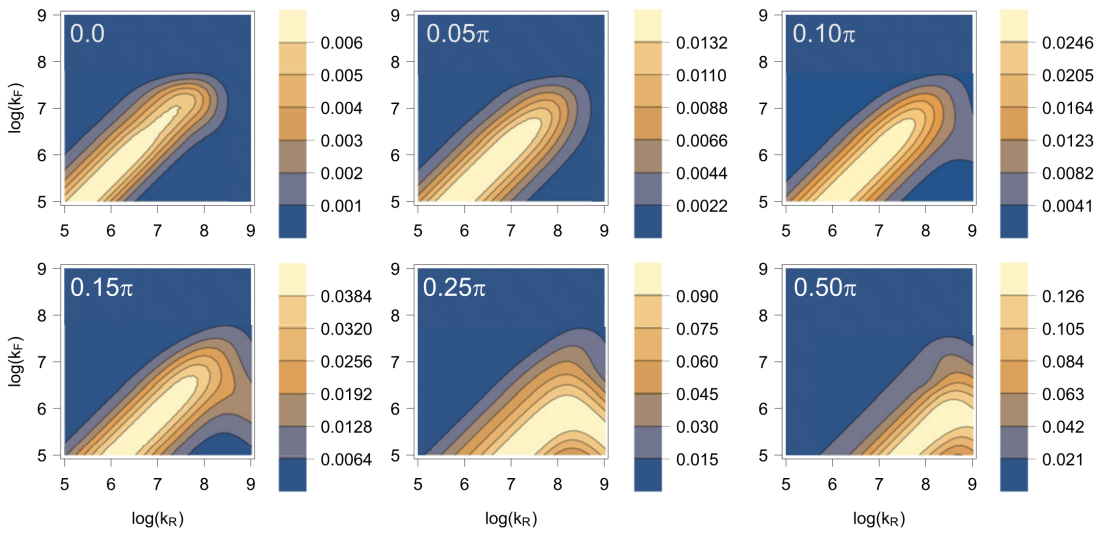


Figure 6.7: Contour plots of the reaction yield anisotropy, $\Delta\Phi_R$, as a function of $\log_{10}(k_R)$ and $\log_{10}(k_F)$ for six values of χ between 0 (no CISS) and $\pi/2$ (100% CISS). The six plots have different scales.

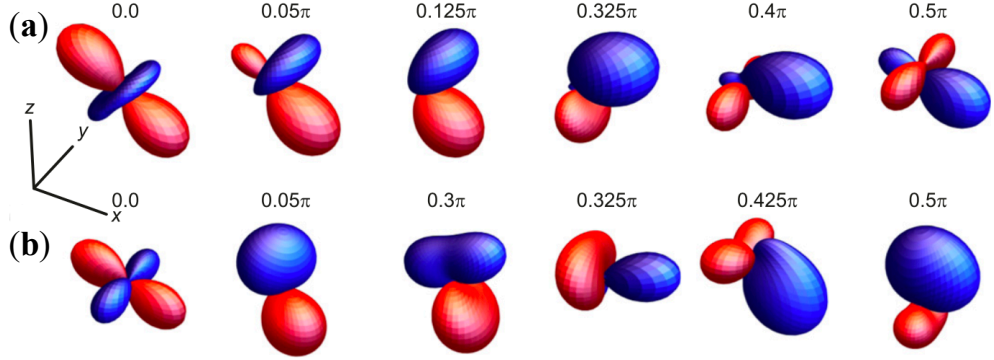


Figure 6.8: Reaction yield anisotropy of the toy radical pair with (a) $k_R = k_F = 10^6 \text{ s}^{-1}$ and (b) $k_R = 10^8 \text{ s}^{-1}$, $k_F = 10^6 \text{ s}^{-1}$ for six representative values of χ between 0 (pure RPM) and $\pi/2$ (pure CISS). These plots are not drawn to scale.

when $\chi = 0$ and $\pi/2$, respectively: $(k_R, k_F) = (10^6, 10^6) \text{ s}^{-1}$ in Figure 6.9(a) and $(k_R, k_F) = (10^8, 10^6) \text{ s}^{-1}$ in Figure 6.8(b). In this representation, the spherical average of the reaction yield, $\langle \Phi_R \rangle$, i.e. the part of Φ_R that is independent of the magnetic field direction, has been subtracted to reveal the anisotropic component, $\bar{\Phi}_R$, which contains the directional information. Red/blue regions correspond to positive/negative $\bar{\Phi}_R$, i.e. reaction yields larger/smaller than $\langle \Phi_R \rangle$. It is clear from Figures 6.8(a) and (b) that the shape of the anisotropy plots is strongly dependent on χ . Surprisingly, the symmetry for Φ_S by reversing the direction of the external magnetic field, i.e. $\bar{\Phi}_S(\theta, \phi) = \bar{\Phi}_S(\theta + \pi, \phi)$, is only found for conventional RPM ($\chi = 0$), and there is a significant anti-symmetric component, $\bar{\Phi}_S(\theta, \phi) - \bar{\Phi}_S(\theta + \pi, \phi)$,

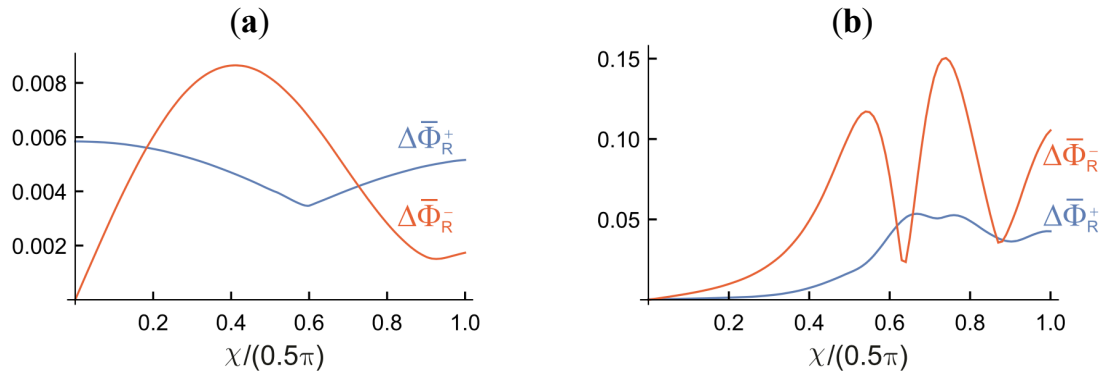


Figure 6.9: Amplitudes of the symmetric and antisymmetric parts of $\bar{\Phi}_R$, as defined in equation (6.25). (a) $k_R = k_F = 10^6 \text{ s}^{-1}$ and (b) $k_R = 10^8 \text{ s}^{-1}$, $k_F = 10^6 \text{ s}^{-1}$.

even for small CISS contributions (e.g. $\chi = 0.05\pi$). The maximum differences in the symmetric and anti-symmetric parts of $\bar{\Phi}_R$ are denoted by $\Delta\bar{\Phi}_R^+$ and $\Delta\bar{\Phi}_R^-$ respectively:

$$\Delta\bar{\Phi}_R^\pm = \frac{1}{2}(\max_{\theta, \phi} \{\bar{\Phi}_{R(\theta, \phi)} \pm \bar{\Phi}_{R(\theta + \pi, \phi)}\} - \min_{\theta, \phi} \{\bar{\Phi}_{R(\theta, \phi)} \pm \bar{\Phi}_{R(\theta + \pi, \phi)}\}), \quad (6.25)$$

which are plotted as a function of χ in Figure 6.9(a) for $k_F = k_R = 10^6 \text{ s}^{-1}$ and Figure 6.9(b) for $k_F = 10^6 \text{ s}^{-1}$ and $k_R = 10^8 \text{ s}^{-1}$.

Time-reversal operation

To understand the asymmetry property of Φ_S for $\chi \neq 0$, we first show the expression of the probability of the recombination-selected state under an external magnetic field $\mathbf{B}_0$:

$$P_{(\mathbf{B}_0, t)}^R = \text{Tr}\{\hat{P}^R \rho_{(\mathbf{B}_0, t)}\} = \frac{1}{Z} \text{Tr}\{\hat{P}^R e^{-i\hat{H}_{(\mathbf{B}_0)}t - \hat{K}_R t} \hat{P}^I e^{i\hat{H}_{(\mathbf{B}_0)}t - \hat{K}_R t}\}, \quad (6.26)$$

where $\hat{H}_{(\mathbf{B}_0)}$ is the Hamiltonian for the magnetic interactions of the two electrons with the internal (hyperfine and dipolar interactions) and external ($\mathbf{B}_0$) fields, and $\hat{K}_R$ characterizes chemical reactions, according to equation (2.),

$$\hat{K}_R = \frac{k_R}{2} \hat{P}^R + \frac{k_F}{2} \hat{\mathbb{1}}. \quad (6.27)$$

Note that without CISS ($\chi = 0$) such that the recombination-selected state is the singlet state,

$$\hat{P}^R = \hat{P}^I = \hat{P}^S, \quad \hat{K}_R = \frac{k_R}{2} \hat{P}^S + \frac{k_F}{2} \hat{\mathbb{1}}, \quad (6.28)$$

and using equation (6.25) with applying the time-reversal operator, $\hat{\Theta}$, gives

$$\begin{aligned} P_{(\mathbf{B}_0, t)}^R &= \text{Tr}\{\hat{\Theta} \hat{P}^S \rho_{(\mathbf{B}_0, t)} \hat{\Theta}^{-1}\} \\ &= \frac{1}{Z} \text{Tr}\{\hat{\Theta} \hat{P}^S e^{-i\hat{H}_{(\mathbf{B}_0)}t - \hat{K}_R t} \hat{P}^S e^{i\hat{H}_{(\mathbf{B}_0)}t - \hat{K}_R t} \hat{\Theta}^{-1}\} \\ &= \frac{1}{Z} \text{Tr}\{\hat{P}^S e^{i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_R t} \hat{P}^S e^{-i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_R t}\} \\ &= \frac{1}{Z} \text{Tr}\{\hat{P}^S e^{-i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_R t} \hat{P}^S e^{i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_R t}\} \\ &= P_{(-\mathbf{B}_0, t)}^R, \end{aligned} \quad (6.29)$$

where the similarity-invariance of the trace, i.e. $\text{Tr}\{A\} = \text{Tr}\{PAP^{-1}\}$ for any square matrix A and any invertible matrix P of the same dimensions, is used, and note that $\hat{P}^S$ and the hyperfine and dipolar interactions contain only bi-linear products of spin operators and are therefore symmetric under time-reversal, and the time-reversal operation on the Zeeman interaction is equivalent to reversing the direction of the magnetic field, so that $\hat{\Theta}\hat{H}_{(\mathbf{B}_0)}\hat{\Theta}^{-1} = \hat{H}_{(-\mathbf{B}_0)}$. Equation (6.28) means that the probability of the recombination-selected (singlet) state, and therefore the recombination yield, is invariant by reversing the direction of the magnetic field for conventional RPM. However, inclusion of CISS ($\chi \neq 0$) makes $\hat{P}^I$ and $\hat{P}^R$ interconverted under time-reversal, because of the $(\hat{S}_{DZ} - \hat{S}_{AZ})$ terms,

$$\hat{\Theta}\hat{P}^I\hat{\Theta}^{-1} = \hat{P}^R, \quad \hat{\Theta}\hat{P}^R\hat{\Theta}^{-1} = \hat{P}^I. \quad (6.30)$$

Then, $P_{(\mathbf{B}_0, t)}^R$ is obtained as

$$\begin{aligned} P_{(\mathbf{B}_0, t)}^R &= \text{Tr}\{\hat{\Theta}\hat{P}^R\rho_{(\mathbf{B}_0, t)}\hat{\Theta}^{-1}\} \\ &= \frac{1}{Z} \text{Tr}\{\hat{\Theta}\hat{P}^R e^{-i\hat{H}_{(\mathbf{B}_0)}t - \hat{K}_R t} \hat{P}^I e^{i\hat{H}_{(\mathbf{B}_0)}t - \hat{K}_R t} \hat{\Theta}^{-1}\} \\ &= \frac{1}{Z} \text{Tr}\{\hat{P}^I e^{i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_I t} \hat{P}^R e^{-i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_I t}\} \\ &= \frac{1}{Z} \text{Tr}\{\hat{P}^R e^{-i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_I t} \hat{P}^I e^{i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_I t}\}, \end{aligned} \quad (6.31)$$

where

$$\hat{\Theta}\hat{K}_R\hat{\Theta}^{-1} = \hat{K}_I, \quad \text{where } \hat{K}_I = \frac{k_R}{2}\hat{P}^I + \frac{k_F}{2}\hat{\mathbb{1}}. \quad (6.32)$$

However, inverting the magnetic field gives

$$P_{(-\mathbf{B}_0, t)}^R = \text{Tr}\{\hat{P}^R\rho_{(-\mathbf{B}_0, t)}\} = \frac{1}{Z} \text{Tr}\{\hat{P}^R e^{-i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_R t} \hat{P}^I e^{i\hat{H}_{(-\mathbf{B}_0)}t - \hat{K}_R t}\}. \quad (6.33)$$

Comparing equations (6.31) and (6.33), we find that $P_{(\mathbf{B}_0, t)}^R$ is not necessarily equal to $P_{(-\mathbf{B}_0, t)}^R$, though the unitary time evolution by the Hamiltonian is equal. Thus, the reaction yields for $\mathbf{B}_0$ and $-\mathbf{B}_0$ are not expected to be equal.

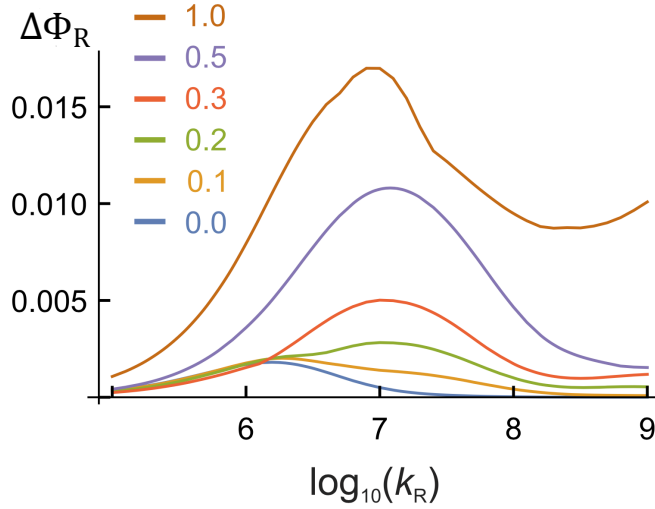


Figure 6.10: Reaction yield anisotropy of the semi-realistic model of the $[\text{FAD}^{\bullet-} \text{Trp}_\text{C}\text{H}^{\bullet+}]$ radical pair in Cry4. $\Delta\Phi_\text{R}$ as a function of k_R for $k_\text{F} = 10^6 \text{ s}^{-1}$ and 6 values of $\chi/(0.5\pi)$.

6.2.2 FAD-TrpH radical pair

Although toy models have the potential to reveal some aspects of the spin dynamics of radical pairs, they can also be misleading. We have therefore performed similar calculations for a semi-realistic model of the $[\text{FAD}^{\bullet-} \text{Trp}_\text{C}\text{H}^{\bullet+}]$ radical pair in Cry4. The two nuclei with the largest anisotropic hyperfine interactions in $\text{FAD}^{\bullet-}$ (nitrogens N5 and N10) and in $\text{Trp}_\text{C}\text{H}^{\bullet+}$ (N1 and its directly bonded proton H1) were included [56, 102]. The relative orientation of the isoalloxazine ring system of the FAD and the indole ring of $\text{Trp}_\text{C}\text{H}$ was taken from the x-ray structure of pigeon Cry4 [134]. As in the case of the toy model, the electron–electron interactions were $D = -0.4 \text{ mT}$ and $J = 0$, and the external magnetic field was again $50 \mu\text{T}$. The dipolar axis, again assumed parallel to the CISS quantization axis, was also taken from the pigeon Cry4 structure [134].

It is clearly shown in Figure 6.10 that the reaction yield anisotropy grows as χ is increased from 0 to $\pi/2$, and its maximum shifts from $k_\text{R} \approx 10^6 \text{ s}^{-1}$ to $k_\text{R} \approx 10^7 \text{ s}^{-1}$ when $k_\text{F} = 10^6 \text{ s}^{-1}$. The latter contrasts with the toy model for

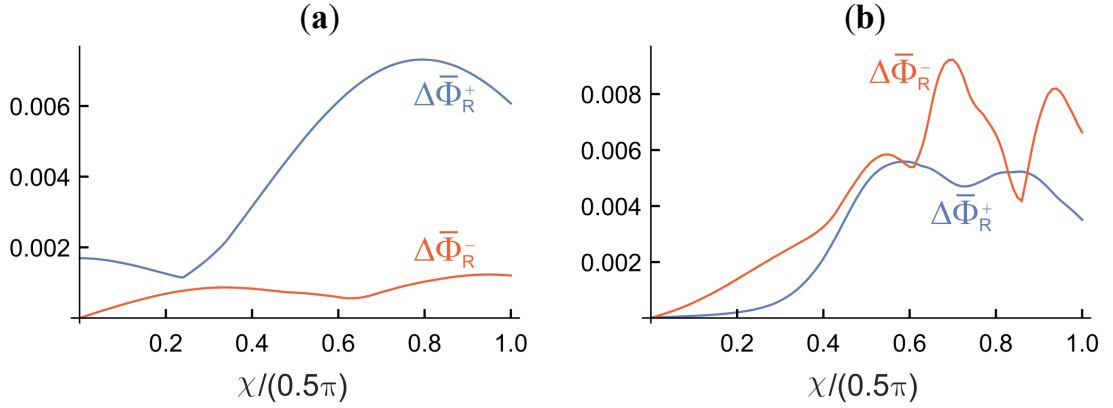


Figure 6.11: Symmetric and anti-symmetric parts of the reaction yields as a function of χ for (a) $k_F = k_R = 10^6 \text{ s}^{-1}$ and (b) $k_F = 10^6 \text{ s}^{-1}$, $k_R = 10^8 \text{ s}^{-1}$.

which the largest anisotropy was found when $k_R \approx 10^8 \text{ s}^{-1}$ (for $\chi = \pi/2$) (Figure 6.7). We attribute this difference to the presence of hyperfine interactions in both radicals which facilitate the double spin-flip, $\alpha_D\beta_A \leftrightarrow \beta_D\alpha_A$, that must take place before recombination can occur (Figure 6.2). Another difference between the two models is that $\Delta\bar{\Phi}_R$ is larger when one radical has no hyperfine interactions (see, e.g. references [102, 209, 210]). Figure 6.11(a) and (b) show the symmetric and antisymmetric parts of $\bar{\Phi}_R$ for $k_R = 10^6 \text{ s}^{-1}$, $k_F = 10^6 \text{ s}^{-1}$ and $k_R = 10^8 \text{ s}^{-1}$, $k_F = 10^6 \text{ s}^{-1}$, respectively. In both cases there is a significant antisymmetric component even for small values of χ , though $\Delta\bar{\Phi}_R^-$ rises as k_R becomes larger than k_F .

One of the many unresolved aspects of the cryptochrome hypothesis is whether radical pair reactions could be sensitive enough to the direction of the geomagnetic field to form the basis of a viable magnetic compass sensor [56, 57, 97, 102, 211]. Factors with the potential to boost the signal are therefore of interest. When radical pairs are formed in, and recombine from, the singlet state ($\chi = 0$), the directional information encoded in the yield of the signalling state arises exclusively from the hyperfine and dipolar interactions. When CISS is present

($\chi \neq 0$), spin-selective initial and reactive states both depend on the direction of the magnetic field in the molecular frame. This additional source of anisotropy results in increases in $\Delta\Phi_{\text{R}}$ that could translate into a more precise compass bearing. Furthermore, the consequence of significant CISS participation in the formation and recombination of radical pairs is that the largest values of $\Delta\Phi_{\text{R}}$ are found when $k_{\text{R}} \gg k_{\text{F}}$ instead of $k_{\text{R}} \approx k_{\text{F}}$. Effective competition between the recombination and forward reactions, requires a larger value of k_{R} to compensate for the time required to reach the reactive $\beta_{\text{D}}\alpha_{\text{A}}$ state. The presence of CISS could, therefore, relax the normal criterion for optimal magnetic sensitivity ($k_{\text{R}} \approx k_{\text{F}}$) giving evolution greater scope for maximising the performance of the compass sensor. One of the arguments in favour of a radical pair magnetosensor over a mechanism based on magnetic nanoparticles is that migratory songbirds are indifferent to the polarity of the magnetic field, instead using the angle between the field direction and the horizontal to distinguish equatorward and poleward directions [15, 24]. This axial compass is distinct from a hypothetical polarity compass based on single-domain crystals of e.g. magnetite, Fe_3O_4 . The observation of polar magnetic responses [212] has been used as an argument against a radical pair sensory mechanism in those species. The projection operators $\hat{P}^{\text{I}}$ and $\hat{P}^{\text{R}}$ used here to merge CISS spin selectivity with the conventional RPM lack time-reversal symmetry so that reaction yields are no longer expected to be even functions of the magnetic field. This is the reason why, as soon as $\chi \neq 0$, we see antisymmetric contributions to the reaction yield anisotropy.

6.3 Conclusion

On the assumption that CISS effects can arise in the electron transfer reactions of organic radical pairs, we have proposed a formulation for merging CISS spin selectivity with that which arises in the conventional RPM. The principal change

in the initial state of a radical pair when CISS effects are included is the spin-polarization term, $\hat{S}_{DZ} - \hat{S}_{AZ}$, which is absent when only the RPM is considered. Because the polarization is quantized along an axis in the molecular frame it should be detectable in measurements on oriented samples, either as differences in continuous wave, time-resolved EPR spectra recorded with the spectrometer field parallel or perpendicular to the CISS axis or as the in-phase signal in an ESEEM experiment. CISS contributions to the EPR spectra of randomly oriented samples are likely to be small. We hope this analysis may stimulate experimental searches for CISS effects in the EPR spectra of radical pairs and be of use to those who may have already embarked on such investigations.

In the context of avian magnetoreception, there are three principal ways in which CISS changes the response of a radical pair to the geomagnetic field. (a) The reaction yield signal that encodes the field direction is more strongly anisotropic and could therefore afford a more precise compass bearing or allow the compass to operate at lower light levels [211]. (b) The signal has a different dependence on the reaction rate constants, and so could give greater scope for evolutionary optimization. (c) In contrast to behavioural experiments showing that migratory songbirds have an axial compass [15, 24], the directional information from a radical pair sensor with a significant CISS component would no longer be invariant to reversal of the magnetic field. Although CISS effects, if they can occur in radical pair reactions, offer the possibility of evolving a more sensitive or precise compass, the associated lack of field-inversion symmetry has not hitherto been observed in behavioural experiments. Additionally, it may no longer be safe to argue that a polar magnetic response in an animal behaviour experiment is evidence against a radical pair mechanism.

Chapter 7

Conclusion

Attributing the avian magnetic-compass sense used for migration over 25000 km to a delicate quantum effect, the radical pair mechanism, is a bold hypothesis. Extensive behavioural studies [1, 12, 14–16] with complementary photo-chemical experiments [53, 79] and quantum mechanical simulations [54, 56, 57, 110] make it promising for this remarkable idea to explain birds’ magnetic sense. Accumulating evidence points to cryptochrome proteins as the most likely candidate magnetoreceptor. In this thesis, we explore possibilities for pronounced influences upon the spin dynamics of photo-induced radical pairs in cryptochromes and here we summarise the main conclusions of this work.

In Chapter 3, we used degenerate perturbation theory to analyse weak magnetic field effects on the eigenstructure of a model radical pair. The anisotropic response to a weak magnetic field with respect to its direction relies on the field-induced reconstruction of the (nearly) degenerate subspaces and effects on coherence dynamics via extra energy-level splitting. Unlike the weak magnetic field effect on radical pairs with isotropic hyperfine interactions, which is based on opening new pathways for S- T_0 interconversion [104], the directional sensitivity to the external magnetic field of a radical pair with axially anisotropic hyperfine interactions, as in the FAD-based radical pairs in cryptochromes, originates in

the modulation of S - $T_{\pm}$ and T_0 - $T_{\pm}$ interconversions. The eigenstructure of a “reference” radical is immune from the external magnetic field no matter how the field is oriented. Such a radical paired with a “probe” radical, whose spin evolution is determined primarily by the external field, gives a “reference-probe” model [102, 105, 106] which greatly accelerates spin dynamics computation. Although inter-radical interactions as strong as hyperfine interactions could abolish the correspondence between the directional sensitivity and the reference character, centre-centre separations larger than ~ 1.7 nm could retain the good reference character of the $\text{FAD}^{\bullet-}$ radical, ensuring the flavin-involved radical pair as an ideal candidate of magnetoreceptor. The reference-probe model still works satisfactorily if the radical paired to the flavin radical has an isotropic internal field environment. However, this is unfortunately what the tryptophan radical lacks.

In Chapter 4, we proposed a convincing test for radical-pair magnetoreception - orientation of birds under a radiofrequency (RF) field in the absence of static fields, rather than disorientation in a static field by RF fields, would provide clear evidence for the direct involvement of radical pairs in the compass magnetoreceptor. Perturbation theory analysis shows that an RF field could remarkably modulate radical-pair spin dynamics via the field-induced resonance. Transitions between eigenstates promote the efficiency of singlet-triplet interconversion, so that the triplet yield of a singlet-born radical pair is increased. Such a zero-field resonance effect requires energy degeneracy of the magnetic interactions in radical pairs, which is satisfied by FAD-based radical pairs. Calculation for FAD-Z radical pairs shows that the resonance effect could be anisotropic with respect to the direction of the monochromatic RF field. The anisotropic response to the RF field is increased to a notable extent when the field strength is increased from ~ 50 μT (geomagnetic field) to ~ 500 μT with the frequency not far exceeding 100 MHz.

A monochromatic RF field at low frequency ~ 1 MHz could cause comparable anisotropy of the reaction yield with that from the geomagnetic (static) field, though the “quantum needle” would not show up. Thus, if birds could orient under an RF field at such low frequency, the role of the needle in avian magnetoreception would then be suspected.

In Chapter 5, we showed that a specific spin relaxation mechanism accounts for the repeatedly detected time-dependent magnetic field effects in CRDS experiments [124, 125]. The “ $B_{1/2}$ ” value, a parameter that characterizes the magnetic field-dependence of the reactions, was found to have a profound time-dependence - an increase from ~ 3 to ~ 7 mT in the pump-probe delay range 0.25 - 10 μ s - for W369F mutants of three avian (robin, chicken and pigeon) Cry4a proteins. Among several possible spin relaxation mechanisms in cryptochromes, only singlet-triplet dephasing (STD), with a relaxation rate constant $\geq 10^7$ s $^{-1}$, could appropriately explain the time-dependence of $B_{1/2}$ without abolishing the change ($\sim 20\%$) in reaction yield brought about by the applied magnetic field. STD could originate in electron hopping between the second and third tryptophans of the tryptophan-tetrad electron transfer chain in Cry4a. Further calculation, including fast electron hopping between the third and fourth tryptophans, shows that STD, at a rate much faster than the chemical reactions, does not seem to destroy the directional sensitivity of the FAD-Trp radical pairs in wild-type Cry4a to the external weak magnetic field.

In Chapter 6, we considered the potential effects of chiral-induced spin selectivity (CISS) [153–165] in the conventional radical pair mechanism. The CISS polarization effects could be observable by electron paramagnetic resonance (EPR) of oriented samples either as differences in continuous wave, time-resolved spectra

recorded with the spectrometer field parallel or perpendicular to the CISS quantization axis or as signals in the in-phase channel of an out-of-phase electron spin echo envelope modulation (ESEEM) experiment. Inclusion of CISS causes greater anisotropic response of the radical-pair reactions to the field direction, so that a more precise compass bearing could be expected. Moreover, CISS relieves the strict condition for a sensitive radical pair magnetoreceptor that the radical-pair reactions must have competing rate constants - even though the radical-pair recombination is ~ 10 times quicker than the spin-independent radical deprotonation, an optimal directional sensitivity could still be realized. Although the associated lack of field-inversion symmetry has not hitherto been observed in behavioural experiments on birds' orientation, the possibility that CISS could play a role in the polarity compass of animals cannot be immediately excluded.

Appendix A

Hyperfine tensors

A.1 FAD radical

Nucleus	A	a_{iso}	T_{qq}
N5	$\begin{pmatrix} -0.0989 & 0.0039 & 0.0 \\ 0.0039 & -0.0881 & 0.0 \\ 0.0 & 0.0 & 1.7569 \end{pmatrix}$	0.5233	$\begin{matrix} 1.2336 \\ -0.6101 \\ -0.6234 \end{matrix}$
N10	$\begin{pmatrix} -0.0190 & -0.0048 & 0.0 \\ -0.0048 & -0.0196 & 0.0 \\ 0.0 & 0.0 & 0.6046 \end{pmatrix}$	0.1887	$\begin{matrix} 0.4159 \\ -0.2031 \\ -0.2128 \end{matrix}$
H6	$\begin{pmatrix} -0.2569 & -0.1273 & 0.0 \\ -0.1273 & -0.4711 & 0.0 \\ 0.0 & 0.0 & -0.4336 \end{pmatrix}$	-0.3872	$\begin{matrix} 0.1896 \\ -0.0464 \\ -0.1432 \end{matrix}$
H8($\times 3$)	$\begin{pmatrix} 0.4399 & 0.0 & 0.0 \\ 0.0 & 0.4399 & 0.0 \\ 0.0 & 0.0 & 0.4399 \end{pmatrix}$	0.4399	$\begin{matrix} 0.0 \\ 0.0 \\ 0.0 \end{matrix}$
H β	$\begin{pmatrix} 0.4070 & 0.0 & 0.0 \\ 0.0 & 0.4070 & 0.0 \\ 0.0 & 0.0 & 0.4070 \end{pmatrix}$	0.4070	$\begin{matrix} 0.0 \\ 0.0 \\ 0.0 \end{matrix}$

Table A.1: The hyperfine tensors for the FAD $^{\bullet-}$ radical.

A.1. FAD radical

The hyperfine tensors of the FAD radical anion (following Ref [102]) were calculated by Dr Ilya Kuprov, Department of Chemistry, University of Southampton, using density functional theory (DFT) in Gaussian-03 at the UB3LYP/EPR-3 level. All hyperfine parameters are in mT. The atom numbering scheme is as shown in Figure A.1.

A: Full hyperfine tensors.

a_{iso} : Isotropic hyperfine interactions.

T_{qq} : Principal anisotropic components of the hyperfine tensors (arranged in descending order of magnitude for each nucleus).

Notes:

H8 *methyl group*: the anisotropic components are small (< 0.08 mT) and were not included in the spin dynamics simulations. The average of the three isotropic couplings, $(0.6493 + 0.6493 + 0.0212)/3$ mT, was used for all three methyl protons on the assumption that methyl group rotation is fast enough to average the three interactions.

H β : the anisotropic components are small (< 0.09 mT) and were not included. One of the β protons was assigned with an isotropic hyperfine coupling equal to the largest of those calculated for the βCH_3 group (0.4070, 0.4070, -0.0189) mT.

A.2 Tryptophan radical

Nucleus	A	a_{iso}	T_{qq}
N1	$\begin{pmatrix} -0.0336 & 0.0924 & -0.1354 \\ 0.0924 & 0.3303 & -0.5318 \\ -0.1354 & -0.5318 & 0.6680 \end{pmatrix}$	0.3215	$\begin{matrix} 0.7596 \\ -0.3745 \\ -0.3851 \end{matrix}$
H1	$\begin{pmatrix} -0.9920 & -0.2091 & -0.2003 \\ -0.2091 & -0.2631 & 0.2803 \\ -0.2003 & 0.2803 & -0.5398 \end{pmatrix}$	-0.5983	$\begin{matrix} 0.5914 \\ -0.1071 \\ -0.4843 \end{matrix}$
H2	$\begin{pmatrix} -0.2843 & 0.1757 & 0.1525 \\ 0.1757 & -0.2798 & 0.0975 \\ 0.1525 & 0.0975 & -0.2699 \end{pmatrix}$	-0.2780	$\begin{matrix} 0.2855 \\ -0.0919 \\ -0.1936 \end{matrix}$
H4	$\begin{pmatrix} -0.5596 & -0.1956 & -0.1657 \\ -0.1956 & -0.4020 & 0.0762 \\ -0.1657 & 0.0762 & -0.5021 \end{pmatrix}$	-0.4880	$\begin{matrix} 0.3001 \\ -0.0480 \\ -0.2520 \end{matrix}$
H6	$\begin{pmatrix} -0.0506 & 0.0622 & 0.0889 \\ 0.0622 & -0.3100 & -0.0297 \\ 0.0889 & -0.0297 & 0.2642 \end{pmatrix}$	-0.2083	$\begin{matrix} 0.1979 \\ -0.0494 \\ -0.1485 \end{matrix}$
H7	$\begin{pmatrix} -0.4355 & -0.1541 & -0.1239 \\ -0.1541 & -0.2777 & 0.0864 \\ -0.1239 & 0.0864 & -0.3770 \end{pmatrix}$	-0.3636	$\begin{matrix} 0.2540 \\ -0.0594 \\ -0.1945 \end{matrix}$
H β	$\begin{pmatrix} 1.5808 & -0.0453 & -0.0506 \\ -0.0453 & 1.5575 & 0.0988 \\ -0.0506 & 0.0988 & 1.6752 \end{pmatrix}$	1.6046	$\begin{matrix} 0.1521 \\ -0.0456 \\ -0.1065 \end{matrix}$

Table A.2: The hyperfine tensors for the TrpH $^{\bullet+}$ radical.

A.2. Tryptophan radical

The hyperfine tensors of the Tryptophan radical anion (following Ref [102]) were calculated by Dr Ilya Kuprov, Department of Chemistry, University of Southampton, using density functional theory (DFT) in Gaussian-03 at the UB3LYP/EPR-3 level. All hyperfine parameters are in mT. The atom numbering scheme is as shown in Figure A.2.

A: Full hyperfine tensors.

a_{iso} : Isotropic hyperfine interactions.

T_{qq} : Principal anisotropic components of the hyperfine tensors (arranged in descending order of magnitude for each nucleus).

Notes:

H β : one of the β proton with the larger isotropic hyperfine interaction (1.6046 mT). The other had a much smaller a_{iso} (0.0457 mT).

Appendix B

Degenerate perturbation treatment for the one-proton radical pair with an isotropic hyperfine interaction

The matrix representation of the Hamiltonian for the hyperfine interaction in radical 1 is

$$\hat{H}_0 = \begin{pmatrix} \frac{a}{4} & 0 & 0 & 0 \\ 0 & -\frac{a}{4} & \frac{a}{2} & 0 \\ 0 & \frac{a}{2} & -\frac{a}{4} & 0 \\ 0 & 0 & 0 & \frac{a}{4} \end{pmatrix}, \quad (\text{B.1})$$

with the four eigenvectors

$$|1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \quad |3^{(0)}\rangle = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, \quad |4^{(0)}\rangle = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, \quad (\text{B.2})$$

and their eigenvalues

$$\omega_1^{(0)} = \omega_2^{(0)} = \omega_3^{(0)} = \frac{a}{4}, \quad \omega_4^{(0)} = -\frac{3a}{4}. \quad (\text{B.3})$$

Note that for this one-proton radical with the isotropic hyperfine interaction, the degenerate subspace is composed of $|1^{(0)}\rangle$, $|2^{(0)}\rangle$ and $|3^{(0)}\rangle$ by contrast with the axial hyperfine interaction case where $|1^{(0)}\rangle$ and $|2^{(0)}\rangle$ construct a degenerate subspace and $|3^{(0)}\rangle$ and $|4^{(0)}\rangle$ construct a nearly degenerate subspace (see Chapter

3). The matrix representation of Hamiltonian for the Zeeman interaction with the weak magnetic field along the z -axis is

$$\delta\hat{H} = \begin{pmatrix} \frac{\omega_0}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_0}{2} & 0 & 0 \\ 0 & 0 & -\frac{\omega_0}{2} & 0 \\ 0 & 0 & 0 & -\frac{\omega_0}{2} \end{pmatrix}. \quad (\text{B.4})$$

Applying degenerate perturbation theory, the perturbed eigenstates and the corresponding eigenvalues are obtained as

$$\begin{aligned} |1'\rangle &= |1^{(0)}\rangle, \quad \omega'_1 = \frac{a}{4} + \frac{\omega_0}{2}, \\ |2'\rangle &= |2^{(0)}\rangle, \quad \omega'_2 = \frac{a}{4} - \frac{\omega_0}{2}, \\ |3'\rangle &= \frac{2a}{\sqrt{4a^2 + \omega_0^2}}|3^{(0)}\rangle + \frac{\omega_0}{\sqrt{4a^2 + \omega_0^2}}|4^{(0)}\rangle, \quad \omega'_3 = \frac{a}{4} + \frac{\omega_0^2}{4a}, \\ |4'\rangle &= \frac{2a}{\sqrt{4a^2 + \omega_0^2}}|4^{(0)}\rangle - \frac{\omega_0}{\sqrt{4a^2 + \omega_0^2}}|3^{(0)}\rangle, \quad \omega'_4 = -\frac{3a}{4} - \frac{\omega_0^2}{4a}. \end{aligned} \quad (\text{B.5})$$

The degeneracy is clearly broken by the weak field. The two eigenstates of radical 2 are

$$|z_+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |z_-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (\text{B.6})$$

and their eigenvalues are $\omega_0/2$ and $-\omega_0/2$. The S and T_0 projection operators are $\hat{P}^S$ and $\hat{P}^{T_0}$ respectively,

$$\begin{aligned} \hat{P}^S &= \frac{1}{2}|\uparrow\downarrow\alpha\rangle\langle\uparrow\downarrow\alpha| + \frac{1}{2}|\downarrow\uparrow\alpha\rangle\langle\downarrow\uparrow\alpha| - \frac{1}{2}|\uparrow\downarrow\alpha\rangle\langle\downarrow\uparrow\alpha| - \frac{1}{2}|\downarrow\uparrow\alpha\rangle\langle\uparrow\downarrow\alpha| \\ &\quad + \frac{1}{2}|\uparrow\downarrow\beta\rangle\langle\uparrow\downarrow\beta| + \frac{1}{2}|\downarrow\uparrow\beta\rangle\langle\downarrow\uparrow\beta| - \frac{1}{2}|\uparrow\downarrow\beta\rangle\langle\downarrow\uparrow\beta| - \frac{1}{2}|\downarrow\uparrow\beta\rangle\langle\uparrow\downarrow\beta|, \\ \hat{P}^{T_0} &= \frac{1}{2}|\uparrow\downarrow\alpha\rangle\langle\uparrow\downarrow\alpha| + \frac{1}{2}|\downarrow\uparrow\alpha\rangle\langle\downarrow\uparrow\alpha| + \frac{1}{2}|\uparrow\downarrow\alpha\rangle\langle\downarrow\uparrow\alpha| + \frac{1}{2}|\downarrow\uparrow\alpha\rangle\langle\uparrow\downarrow\alpha| \\ &\quad + \frac{1}{2}|\uparrow\downarrow\beta\rangle\langle\uparrow\downarrow\beta| + \frac{1}{2}|\downarrow\uparrow\beta\rangle\langle\downarrow\uparrow\beta| + \frac{1}{2}|\uparrow\downarrow\beta\rangle\langle\downarrow\uparrow\beta| + \frac{1}{2}|\downarrow\uparrow\beta\rangle\langle\uparrow\downarrow\beta|. \end{aligned} \quad (\text{B.7})$$

The S and T_0 yields for the singlet-born radical pair are calculated by

$$\Phi_S = \frac{1}{2} \sum_{n,m} P_{nm}^S P_{mn}^S f(\omega_{nm}), \quad \Phi_{T_0} = \frac{1}{2} \sum_{n,m} P_{nm}^{T_0} P_{mn}^S f(\omega_{nm}), \quad (\text{B.8})$$

where $\omega_{nm} = \omega_n - \omega_m$ is the energy gap between two radical-pair eigenstates, and $f_{(\omega_{nm})}$ is the Lorentzian function. In $\mathcal{H}^{123} \otimes \mathcal{H}_{r2}$, electron spins are anti-parallel in the following eigenstates:

$$\begin{aligned} |3'; z_+\rangle &\stackrel{\text{eff}}{=} \frac{1}{\sqrt{2}} \times \frac{2a - \omega_0}{\sqrt{4a^2 + \omega_0^2}} |\downarrow\uparrow \alpha\rangle, \\ |3'; z_-\rangle &\stackrel{\text{eff}}{=} \frac{1}{\sqrt{2}} \times \frac{2a + \omega_0}{\sqrt{4a^2 + \omega_0^2}} |\uparrow\downarrow \beta\rangle, \\ |1'; z_-\rangle &= |\uparrow\downarrow \alpha\rangle, \\ |2'; z_+\rangle &= |\downarrow\uparrow \beta\rangle, \end{aligned} \quad (\text{B.9})$$

and the non-zero coherences in $\hat{P}^S$ and $\hat{P}^{T_0}$ are

$$\begin{aligned} P_{3'z_-, 2'z_+}^S &= -P_{3'z_-, 2'z_+}^{T_0} = -\frac{1}{2\sqrt{2}} \times \frac{2a + \omega_0}{\sqrt{4a^2 + \omega_0^2}}, \\ P_{3'z_+, 1'z_-}^S &= -P_{3'z_+, 1'z_-}^{T_0} = -\frac{1}{2\sqrt{2}} \times \frac{2a - \omega_0}{\sqrt{4a^2 + \omega_0^2}}. \end{aligned} \quad (\text{B.10})$$

Hence, combining equations (B.2-B.8), the perturbative $\Delta\Phi_S$ and $\Delta\Phi_{T_0}$, i.e. change in S and T_0 yields by the magnetic field, are obtained as

$$\begin{aligned} \Delta\Phi_S &= \frac{1}{2} \times 2 \times \left(P_{3'z_-, 2'z_+}^S P_{2'z_+, 3'z_-}^S f_{(\frac{\omega_0^2}{4a} - \frac{\omega_0}{2})} + P_{3'z_+, 1'z_-}^S P_{1'z_-, 3'z_+}^S f_{(\frac{\omega_0^2}{4a} + \frac{\omega_0}{2})} \right) \\ &\quad - \frac{1}{2} \times 2 \times \left(P_{3^{(0)}z_-, 2^{(0)}z_+}^S P_{2^{(0)}z_+, 3^{(0)}z_-}^S f_{(\omega_3^{(0)} - \omega_2^{(0)})} \right. \\ &\quad \left. + P_{3^{(0)}z_+, 1^{(0)}z_-}^S P_{1^{(0)}z_-, 3^{(0)}z_+}^S f_{(\omega_3^{(0)} - \omega_1^{(0)})} \right) \\ &\approx \frac{1}{8} \times \left(\frac{(2a + \omega_0^2)^2}{4a^2 + \omega_0^2} f_{(\frac{\omega_0^2}{4a} - \frac{\omega_0}{2})} + \frac{(2a - \omega_0^2)^2}{4a^2 + \omega_0^2} f_{(\frac{\omega_0^2}{4a} + \frac{\omega_0}{2})} \right) - \frac{1}{4}, \\ \Delta\Phi_{T_0} &= \frac{1}{2} \times 2 \times \left(P_{3'z_-, 2'z_+}^{T_0} P_{2'z_+, 3'z_-}^S f_{(\frac{\omega_0^2}{4a} - \frac{\omega_0}{2})} + P_{3'z_+, 1'z_-}^{T_0} P_{1'z_-, 3'z_+}^S f_{(\frac{\omega_0^2}{4a} + \frac{\omega_0}{2})} \right) \\ &\quad - \frac{1}{2} \times 2 \times \left(P_{3^{(0)}z_-, 2^{(0)}z_+}^{T_0} P_{2^{(0)}z_+, 3^{(0)}z_-}^S f_{(\omega_3^{(0)} - \omega_2^{(0)})} \right. \\ &\quad \left. + P_{3^{(0)}z_+, 1^{(0)}z_-}^{T_0} P_{1^{(0)}z_-, 3^{(0)}z_+}^S f_{(\omega_3^{(0)} - \omega_1^{(0)})} \right) \\ &\approx -\frac{1}{8} \times \left(\frac{(2a + \omega_0^2)^2}{4a^2 + \omega_0^2} f_{(\frac{\omega_0^2}{4a} - \frac{\omega_0}{2})} + \frac{(2a - \omega_0^2)^2}{4a^2 + \omega_0^2} f_{(\frac{\omega_0^2}{4a} + \frac{\omega_0}{2})} \right) + \frac{1}{4}. \end{aligned} \quad (\text{B.11})$$

Note that $\Delta\Phi_S = -\Delta\Phi_{T_0}$ so that $\Delta\Phi_{T_\pm} = 0$. In the limit $a \gg \omega_0$, equation (B.11) can be further simplified as

$$\Delta\Phi_S = -\Delta\Phi_{T_0} = \frac{k^2}{4k^2 + \omega_0^2} - \frac{1}{4}. \quad (\text{B.12})$$

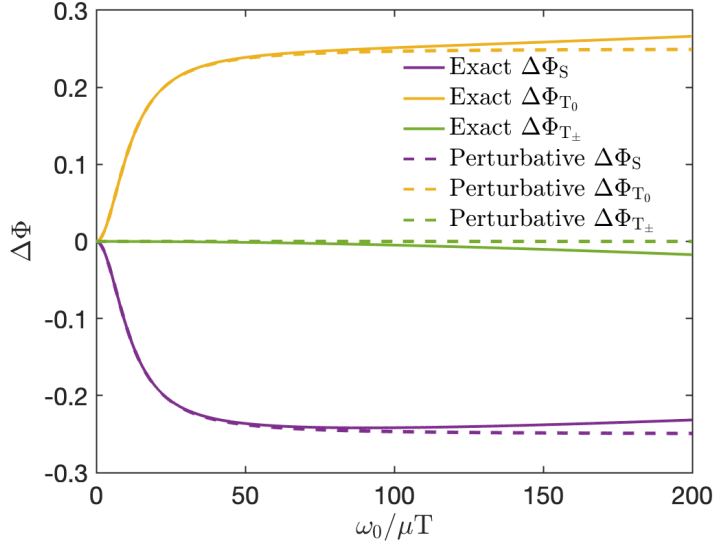


Figure B.1: $\Delta\Phi_S$, $\Delta\Phi_{T_0}$ and $\Delta\Phi_{T_\pm}$ calculated using the exact simulation and the perturbation treatment result in equation (B.12) for the one-proton radical pair with the isotropic hyperfine interaction $a = 500 \mu\text{T}$. The reaction rate constant $k = 10^6 \text{ s}^{-1}$. The external magnetic field ω_0 varies from 0 to 200 μT .

The perturbation treatment result in equation (B.12) agrees satisfactorily with the exact simulation (Figure B.1), indicating that the effect of the weak magnetic field on the coherence dynamics in the degenerate subspace $\mathcal{H}^{123} \otimes \mathcal{H}_{r2}$ opens new pathways for the S- T_0 interconversion. This is consistent with the previous study [104].

Appendix C

Time-dependent perturbation theory

Interaction picture

Consider a Hamiltonian, $\hat{H}$:

$$\hat{H} = \hat{H}_0 + \hat{H}_{1(t)}, \quad (\text{C.1})$$

where $\hat{H}_0$ is the time-independent part that normally has a well-defined spectrum, while $\hat{H}_{1(t)}$ contains the explicitly time-dependent term. Denote a state in the Schrödinger picture as $|\psi_{(t)}\rangle$ and as $|\tilde{\psi}_{(t)}\rangle$ in the interaction picture, so that

$$|\tilde{\psi}_{(t)}\rangle = \mathcal{U}_{0(t)}^\dagger |\psi_{(t)}\rangle = e^{i\hat{H}_0 t} |\psi_{(t)}\rangle, \quad (\text{C.2})$$

where $\mathcal{U}_{0(t)} = e^{-i\hat{H}_0 t}$ is the unitary time-evolution operator for $\hat{H}_0$. Remembering the Schrödinger equation,

$$i \frac{d}{dt} |\psi_{(t)}\rangle = \hat{H} |\psi_{(t)}\rangle, \quad (\text{C.3})$$

gives the dynamical equation for $|\tilde{\psi}_{(t)}\rangle$:

$$\begin{aligned} i \frac{d}{dt} |\tilde{\psi}_{(t)}\rangle &= -i\hat{H}_0 |\tilde{\psi}_{(t)}\rangle + e^{i\hat{H}_0 t} (\hat{H}_0 + \hat{H}_{1(t)}) |\psi_{(t)}\rangle \\ &= -i\hat{H}_0 |\tilde{\psi}_{(t)}\rangle + e^{i\hat{H}_0 t} (\hat{H}_0 + \hat{H}_{1(t)}) e^{-i\hat{H}_0 t} |\tilde{\psi}_{(t)}\rangle \\ &= \hat{\hat{H}}_{1(t)} |\tilde{\psi}_{(t)}\rangle, \end{aligned} \quad (\text{C.4})$$

where $\hat{\hat{H}}_{1(t)} = \mathcal{U}_{0(t)}^\dagger \hat{H}_{1(t)} \mathcal{U}_{0(t)}$.

Perturbation treatment

In many situations, $\hat{H}_{1(t)}$ is small so as a perturbation to $\hat{H}_0$. We then introduce “ λ ” to denote the order of the perturbation, so that

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_{1(t)}, \quad (\text{C.5})$$

and equation (C.4) becomes

$$i \frac{d}{dt} |\tilde{\psi}_{(t)}\rangle = \lambda \hat{H}_{1(t)} |\tilde{\psi}_{(t)}\rangle. \quad (\text{C.6})$$

Expanding $|\tilde{\psi}_{(t)}\rangle$ in the power of λ gives

$$|\tilde{\psi}_{(t)}\rangle = |\tilde{\psi}_{(t)}^{(0)}\rangle + \lambda |\tilde{\psi}_{(t)}^{(1)}\rangle + \lambda^2 |\tilde{\psi}_{(t)}^{(2)}\rangle + \mathcal{O}(\lambda^3). \quad (\text{C.7})$$

Inserting this into equation (C.6) gives

$$\begin{aligned} & i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(0)}\rangle + \lambda i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(1)}\rangle + \lambda^2 i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(2)}\rangle + \lambda^3 i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(3)}\rangle + \mathcal{O}(\lambda^4) \\ &= \lambda \hat{H}_{1(t)} |\tilde{\psi}_{(t)}^{(0)}\rangle + \lambda^2 \hat{H}_{1(t)} |\tilde{\psi}_{(t)}^{(1)}\rangle + \lambda^3 \hat{H}_{1(t)} |\tilde{\psi}_{(t)}^{(2)}\rangle + \mathcal{O}(\lambda^4). \end{aligned} \quad (\text{C.8})$$

The coefficient of each power of λ must vanish, so that

$$i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(0)}\rangle = 0 \quad (\text{C.9a})$$

$$i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(1)}\rangle = \hat{H}_{1(t)} |\tilde{\psi}_{(t)}^{(0)}\rangle \quad (\text{C.9b})$$

$$i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(2)}\rangle = \hat{H}_{1(t)} |\tilde{\psi}_{(t)}^{(1)}\rangle \quad (\text{C.9c})$$

$$\vdots \quad (\text{C.9d})$$

$$i \frac{d}{dt} |\tilde{\psi}_{(t)}^{(n+1)}\rangle = \hat{H}_{1(t)} |\tilde{\psi}_{(t)}^{(n)}\rangle. \quad (\text{C.9e})$$

Equation (C.9a) indicates the time-independence of $|\tilde{\psi}_{(t)}^{(0)}\rangle$, so that

$$|\tilde{\psi}_{(t)}^{(0)}\rangle = |\tilde{\psi}_{(0)}^{(0)}\rangle = |\psi_{(0)}\rangle. \quad (\text{C.10})$$

Then, using equation (C.9b), first-order $|\tilde{\psi}_{(t)}^{(1)}\rangle$ is obtained as

$$|\tilde{\psi}_{(t)}^{(1)}\rangle = -i \int_0^t \hat{H}_{1(t')} |\psi_{(0)}\rangle dt'. \quad (\text{C.11})$$

Higher-order kets are obtained recurrently, e.g. second-order $|\tilde{\psi}_{(t)}^{(2)}\rangle$ is

$$|\tilde{\psi}_{(t)}^{(2)}\rangle = - \int_0^t \hat{H}_{1(t')} dt' \int_0^{t'} \hat{H}_{1(t'')} |\psi_{(0)}\rangle dt''. \quad (\text{C.12})$$

In the eigenbasis of $\hat{H}_0$,

$$\tilde{c}_{n(t)}^{(k)} = \langle n | \tilde{\psi}_{(t)}^{(k)} \rangle, \quad (\text{C.13})$$

where $|n\rangle$ is an eigenstate of $\hat{H}_0$. Then, first-order $\tilde{c}_{n(t)}^{(1)}$ is obtained as

$$\begin{aligned} \tilde{c}_{n(t)}^{(1)} &= -i \int_0^t \langle n | \hat{H}_{1(t')} | \psi_{(0)} \rangle dt' \\ &= -i \int_0^t \langle n | e^{i\hat{H}_0 t} \hat{H}_{1(t')} e^{-i\hat{H}_0 t} | \psi_{(0)} \rangle dt' \\ &= -i \int_0^t \sum_m e^{i\omega_{nm} t} H_{1(t')nm} c_m dt', \end{aligned} \quad (\text{C.14})$$

where $\omega_{nm} = \omega_n - \omega_m$ in which ω_n and ω_m are the corresponding eigenvalues of $|n\rangle$ and $|m\rangle$, $H_{1(t')nm} = \langle n | \hat{H}_{1(t')} | m \rangle$ and $c_m = \langle m | \psi_{(0)} \rangle$.

Appendix D

Inclusion of spin dynamics of the $[\text{FAD}^{\bullet-} \text{ Trp}^{\bullet}]$ radical pair

The reaction scheme is shown in Figure . RP1 denotes the $[\text{FAD}^{\bullet-} \text{ TrpH}^{\bullet+}]$ radical pair, and RP2 denotes the $[\text{FAD}^{\bullet-} \text{ Trp}^{\bullet}]$ radical pair. The Liouvillian superoperators of RP1 and RP2 are:

$$\begin{aligned}\hat{\hat{L}}_1 &= i(\hat{H}_1 \otimes \hat{\mathbb{1}} - \hat{\mathbb{1}} \otimes \hat{H}_1^\top) + \frac{k_r}{2} \hat{\hat{Q}}_S + k_f \hat{\mathbb{1}} + \hat{\hat{W}}_1, \\ \hat{\hat{L}}_2 &= i(\hat{H}_2 \otimes \hat{\mathbb{1}} - \hat{\mathbb{1}} \otimes \hat{H}_2^\top) + \frac{k_b}{2} \hat{\hat{Q}}_S + k_p \hat{\mathbb{1}} + \hat{\hat{W}}_2,\end{aligned}\tag{D.1}$$

where $\hat{H}_1$ and $\hat{H}_2$ are the Hamiltonians of RP1 and RP2, $\hat{\hat{Q}}_S = \hat{P}^S \otimes \hat{\mathbb{1}} + \hat{\mathbb{1}} \otimes \hat{P}^S$ characterizes the radical-pair recombination, $\hat{\mathbb{1}} = \hat{\mathbb{1}} \otimes \hat{\mathbb{1}}$ represents the spin-independent reactions, and $\hat{\hat{W}}_1$ and $\hat{\hat{W}}_2$ denote the spin relaxations for RP1 and RP2. The dynamical equations for the density operators of RP1 and RP2 in Liouville space are

$$\frac{d\sigma_{1(t)}}{dt} = -\hat{\hat{L}}_1 \sigma_{1(t)},\tag{D.2a}$$

$$\frac{d\sigma_{2(t)}}{dt} = -\hat{\hat{L}}_2 \sigma_{2(t)} + k_f \sigma_{1(t)}.\tag{D.2b}$$

The solution of equation (D.2a) is obtained as

$$\sigma_{1(t)} = e^{-\hat{\hat{L}}_1 t} \sigma_{1(0)}.\tag{D.3}$$

Substituting equation (D.3) into (D.2b) gives

$$e^{\hat{\hat{L}}_2 t} \frac{d\sigma_{2(t)}}{dt} + e^{\hat{\hat{L}}_2 t} \hat{\hat{L}}_2 \sigma_{2(t)} = k_f e^{\hat{\hat{L}}_2 t} e^{-\hat{\hat{L}}_1 t} \sigma_{1(0)},\tag{D.4}$$

where both sides are multiplied by $e^{\hat{L}_2 t}$. One finds that the left side of equation (D.4) is the time-derivative of $e^{\hat{L}_2 t} \sigma_{2(t)}$. Integrating both sides by time gives

$$\left[e^{\hat{L}_2 t'} \sigma_{2(t')} \right] \Big|_0^t = k_f \int_0^t e^{\hat{L}_2 t'} e^{-\hat{L}_1 t'} \sigma_{1(0)} dt'. \quad (\text{D.5})$$

Given that $\sigma_{2(0)} = 0$, the solution for $\sigma_{2(t)}$ is obtained as

$$\sigma_{2(t)} = k_f e^{-\hat{L}_2 t} \int_0^t e^{\hat{L}_2 t'} e^{-\hat{L}_1 t'} \sigma_{1(0)} dt'. \quad (\text{D.6})$$

Diagonalization of $\hat{L}_1$ gives

$$e^{-\hat{L}_1 t} = A e^{-\lambda_1 t} A^{-1}, \quad (\text{D.7})$$

where $\lambda_1 = A^{-1} \hat{L}_1 A$. Using equation (D.7) and remembering equation (D.3) allow us to re-write $\sigma_{1(t)}$:

$$\sigma_{1(t)} = \sum_k \mathbf{b}_k e^{-\lambda_{1k} t}, \quad (\text{D.8})$$

where λ_{1k} is the k -th diagonal element of λ_1 , and $\mathbf{b}$ is an aggregate of (column) vectors with the j -th entry of the k -vector is

$$(\mathbf{b}_k)_j = \sum_m A_{jk} (A^{-1})_{km} (\sigma_{1(0)})_m, \quad (\text{D.9})$$

in which $(\sigma_{1(0)})_m$ is the m -th entry of (vector) $\sigma_{1(0)}$. Combining equations (D.6-D.9) gives

$$\begin{aligned} \sigma_{2(t)} &= k_f e^{-\hat{L}_2 t} \sum_k \int_0^t e^{\hat{L}_2 t'} e^{-\lambda_{1k} t'} dt' \mathbf{b}_k \\ &= k_f e^{-\hat{L}_2 t} \sum_k \left[e^{(\hat{L}_2 - \lambda_{1k} \hat{\mathbb{I}}) t'} (\hat{L}_2 - \lambda_{1k} \hat{\mathbb{I}})^{-1} \right] \Big|_0^t \mathbf{b}_k \\ &= k_f e^{-\hat{L}_2 t} \sum_k (e^{(\hat{L}_2 - \lambda_{1k} \hat{\mathbb{I}}) t} - \hat{\mathbb{I}}) (\hat{L}_2 - \lambda_{1k} \hat{\mathbb{I}})^{-1} \mathbf{b}_k \\ &= k_f \sum_k (e^{-\lambda_{1k} \hat{\mathbb{I}} t} - e^{-\hat{L}_2 t}) (\hat{L}_2 - \lambda_{1k} \hat{\mathbb{I}})^{-1} \mathbf{b}_k. \end{aligned} \quad (\text{D.10})$$

Then, the remaining (time-dependent) RP1 and RP2, $\Phi_{\text{RP1}(t)}$ and $\Phi_{\text{RP2}(t)}$, are

$$\Phi_{\text{RP1}(t)} = (\sigma_{\mathbf{I}})^{\top} \sigma_{1(t)}, \quad \Phi_{\text{RP2}(t)} = (\sigma_{\mathbf{I}})^{\top} \sigma_{2(t)}, \quad (\text{D.11})$$

where $\sigma_{\mathbf{I}}$ is the row-wise flattened (vectorised) form of the identity matrix $\hat{\mathbb{1}}$ and “ $\mathbf{T}$ ” means transpose. The accumulation of the long-lived $\text{FAD}^{\bullet-}$ radical, $\Phi_{\text{FAD}^{\bullet-}(t)}$, is obtained as

$$\begin{aligned}\Phi_{\text{FAD}^{\bullet-}(t)} &= k_{\text{p}} \int_0^t (\sigma_{\mathbf{I}})^{\text{T}} \sigma_{2(t')} dt' \\ &= k_{\text{p}} k_{\text{f}} (\sigma_{\mathbf{I}})^{\text{T}} \sum_k \left(\lambda_{1k}^{-1} (\hat{\mathbb{1}} - e^{-\lambda_{1k} \hat{\mathbb{1}} t}) - \hat{L}_2^{-1} (\hat{\mathbb{1}} - e^{-\hat{L}_2 t}) \right) (\hat{L}_2 - \lambda_{1k} \hat{\mathbb{1}})^{-1} \mathbf{b}_k.\end{aligned}\tag{D.12}$$

Appendix E

Non-Hermitian perturbation treatment

The new operator $\hat{\mathcal{K}}$ including the spin interactions and the singlet-triplet dephasing is written,

$$\hat{\mathcal{K}} = \hat{\mathcal{M}} + \hat{\mathcal{Q}}, \quad (\text{E.1})$$

with

$$\hat{\mathcal{M}} = \begin{pmatrix} r & -\omega & 0 \\ \omega & r & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{\mathcal{Q}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -q \\ 0 & q & 0 \end{pmatrix}. \quad (\text{E.2})$$

Note that $\hat{\mathcal{K}}$, $\hat{\mathcal{M}}$ and $\hat{\mathcal{Q}}$ are all non-Hermitian. Treating $\hat{\mathcal{Q}}$ as a perturbation to $\hat{\mathcal{M}}$, as $q^2 \ll \omega^2 + r^2$, we find the eigenvectors of $\hat{\mathcal{M}}$, noted with zero-order superscript, are orthogonal to each other:

$$|1^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad |2^{(0)}\rangle = \begin{pmatrix} -i/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, \quad |3^{(0)}\rangle = \begin{pmatrix} i/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, \quad (\text{E.3})$$

with eigenvalues, $v_1^{(0)} = 0$, $v_2^{(0)} = r - i\omega$ and $v_3^{(0)} = r + i\omega$. Introducing “ λ ” to characterize the orders of the perturbation, then $\hat{\mathcal{K}}$ is a function of λ , written as $\hat{\mathcal{K}}_{(\lambda)} = \hat{\mathcal{M}} + \lambda \hat{\mathcal{Q}}$. Thus, the eigenvectors and eigenvalues of $\hat{\mathcal{K}}_{(\lambda)}$ can be written as a function of λ ,

$$\hat{\mathcal{K}}_{(\lambda)}|n\rangle_\lambda = v_{n(\lambda)}|n\rangle_\lambda, \quad \text{with } n = 1, 2, 3. \quad (\text{E.4})$$

Specially, if $\lambda = 0$, $\hat{\mathcal{K}}_{(\lambda)}$ is reduced to $\hat{\mathcal{M}}$, and the eigenvectors and eigenvalues are: $|n\rangle_{\lambda=0} = |n^{(0)}\rangle$ and $v_{n(\lambda)} = v_n^{(0)}$. Now, expanding $|n\rangle_{\lambda}$ and $v_{n(\lambda)}$ with respect to λ , we have:

$$\begin{aligned} |n\rangle_{\lambda} &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots, \\ v_{n(\lambda)} &= v_n^{(0)} + \lambda v_n^{(1)} + \lambda^2 v_n^{(2)} + \dots. \end{aligned} \quad (\text{E.5})$$

Knowing that equation (E.4) is equivalent to $(\hat{\mathcal{M}} + \lambda \hat{\mathcal{Q}} - v_{n(\lambda)})|n\rangle_{\lambda} = 0$ and substituting equation (E.5) give:

$$\begin{aligned} \left((\hat{\mathcal{M}} - v_n^{(0)}) - \lambda(v_n^{(1)} - \hat{\mathcal{Q}}) - \lambda^2 v_n^{(2)} - \dots - \lambda^k v_n^{(k)} - \dots \right) (|n^{(0)}\rangle + \\ \lambda |n^{(1)}\rangle + \dots + \lambda^k |n^{(k)}\rangle \dots) = 0. \end{aligned} \quad (\text{E.6})$$

Collecting the coefficients for each power of λ , we have:

$$\begin{aligned} \lambda^0 : (\hat{\mathcal{M}} - v_n^{(0)})|n^{(0)}\rangle &= 0, \\ \lambda^1 : (\hat{\mathcal{M}} - v_n^{(0)})|n^{(1)}\rangle &= (v_n^{(1)} - \hat{\mathcal{Q}})|n^{(0)}\rangle, \\ \lambda^2 : (\hat{\mathcal{M}} - v_n^{(0)})|n^{(2)}\rangle &= (v_n^{(1)} - \hat{\mathcal{Q}})|n^{(1)}\rangle + v_n^{(2)}|n^{(0)}\rangle, \\ &\vdots \\ \lambda^k : (\hat{\mathcal{M}} - v_n^{(0)})|n^{(k)}\rangle &= (v_n^{(1)} - \hat{\mathcal{Q}})|n^{(k-1)}\rangle + v_n^{(2)}|n^{(k-2)}\rangle + \dots + v_n^{(k)}|n^{(0)}\rangle, \\ &\vdots \end{aligned} \quad (\text{E.7})$$

It is appropriate to assume that all the eigenvector corrections $|n^{(j)}\rangle$, with $j > 1$, are orthogonal to $|n^{(0)}\rangle$ without loss of generality [85]. For λ^1 , applying $\langle n^{(0)}|$, we have:

$$\langle n^{(0)}|(\hat{\mathcal{M}} - v_n^{(0)})|n^{(1)}\rangle = \langle n^{(0)}|(v_n^{(1)} - \hat{\mathcal{Q}})|n^{(0)}\rangle. \quad (\text{E.8})$$

Since,

$$\begin{aligned} \langle 1^{(0)}|\hat{\mathcal{M}} &= (\hat{\mathcal{M}}^\dagger|1^{(0)}\rangle)^\dagger = (v_1^{(0)}|1^{(0)}\rangle)^\dagger = v_1^{(0)}\langle 1^{(0)}|, \\ \langle 2^{(0)}|\hat{\mathcal{M}} &= (\hat{\mathcal{M}}^\dagger|2^{(0)}\rangle)^\dagger = ((r + i\omega)|2^{(0)}\rangle)^\dagger = v_2^{(0)}\langle 2^{(0)}|, \\ \langle 3^{(0)}|\hat{\mathcal{M}} &= (\hat{\mathcal{M}}^\dagger|3^{(0)}\rangle)^\dagger = ((r - i\omega)|3^{(0)}\rangle)^\dagger = v_3^{(0)}\langle 3^{(0)}|, \end{aligned} \quad (\text{E.9})$$

the first-order corrections to the eigenvalues are all zero, as

$$v_n^{(1)} = \langle n^{(0)}|\hat{\mathcal{Q}}|n^{(0)}\rangle = 0. \quad (\text{E.10})$$

In order to obtain the first-order corrections to the eigenvectors, we apply $\langle m^{(0)}|$ with $m \neq n$:

$$(v_m^{(0)} - v_n^{(0)}) \langle m^{(0)} | n^{(1)} \rangle = -\mathcal{Q}_{mn} \quad (\text{E.11})$$

where $\mathcal{Q}_{mn} = \langle m^{(0)} | \hat{\mathcal{Q}} | n^{(0)} \rangle$. Thus,

$$|n^{(1)}\rangle = \sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)} | n^{(1)} \rangle = \sum_{m \neq n} \frac{-\mathcal{Q}_{mn}}{v_m^{(0)} - v_n^{(0)}} |m^{(0)}\rangle. \quad (\text{E.12})$$

Therefore,

$$|1^{(1)}\rangle = \begin{pmatrix} \frac{\omega\Omega^2}{q} \\ \frac{r\Omega^2}{q} \\ 0 \end{pmatrix}, \quad |2^{(1)}\rangle = \begin{pmatrix} 0 \\ 0 \\ \frac{\Omega^2(r+i\omega)}{\sqrt{2}q} \end{pmatrix}, \quad |3^{(1)}\rangle = \begin{pmatrix} 0 \\ 0 \\ \frac{\Omega^2(r-i\omega)}{\sqrt{2}q} \end{pmatrix}, \quad (\text{E.13})$$

where $\Omega^2 = q^2/(r^2 + \omega^2)$. Furthermore, the second-order corrections to the eigenvalues are obtained by applying $\langle n^{(0)}|$ to the λ^2 equation in (E.7):

$$v_n^{(2)} = \langle n^{(0)} | \hat{\mathcal{Q}} | n^{(1)} \rangle = \sum_{m \neq n} \frac{-\langle n^{(0)} | \hat{\mathcal{Q}} | m^{(0)} \rangle \mathcal{Q}_{mn}}{v_m^{(0)} - v_n^{(0)}} = \sum_{m \neq n} \frac{-|\mathcal{Q}_{mn}|^2}{v_m^{(0)} - v_n^{(0)}}. \quad (\text{E.14})$$

Thus,

$$v_1^{(2)} = r\Omega^2, \quad v_2^{(2)} = -\frac{1}{2}\Omega^2(r + i\omega), \quad v_3^{(2)} = -\frac{1}{2}\Omega^2(r - i\omega). \quad (\text{E.15})$$

Appendix F

STD induced enhancement of directional magnetic-field sensitivity

A weak magnetic field modulates the radical-pair spin dynamics, through the change in the (nearly) degenerate spin subspaces (see Chapter 3), anisotropically with respect to its orientations. For a simple one-proton radical pair with an axial hyperfine interaction, the S-T_± interconversion, driven by the small x , y components of the hyperfine interaction, is characterized in (nearly) degenerate subspaces of spin Hamiltonian (e.g. $\mathcal{H}^{34}$ constructed by $|3^{(0)}\rangle$, $|4^{(0)}\rangle$ in equation (3.4)). It is in these subspaces that the S-T_± interconversion is possibly affected by the weak field to a remarkable extent. Reducing the four electron spin states (S, T₀, T₊, T₋) to a two-level system (S, T₊) gives the simplified spin Hamiltonian with the matrix form:

$$\hat{H}_0 = \begin{pmatrix} a/4 + d & \varepsilon/2 \\ \varepsilon/2 & a/4 \end{pmatrix}, \quad (\text{F.1})$$

where a denotes the z -component hyperfine interaction where S, T₊ are degenerate, ε denotes the x , y -component hyperfine interaction responsible for the S-T₊ interconversion, and v characterizes the energy gap introduced by the inter-radical spin interactions. Note that the state kets for S and T₊ are written,

$$|S\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad |T_+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \quad (\text{F.2})$$

Weak magnetic field along the z -axis

The weak magnetic field along the z -axis is represented as,

$$\hat{H}_1^z = \begin{pmatrix} \omega & 0 \\ 0 & 0 \end{pmatrix}. \quad (\text{F.3})$$

Then, the total Hamiltonian is $\hat{H} = \hat{H}_0 + \hat{H}_1^z$. The commutation superoperator of $\hat{H}$ has the matrix form

$$\hat{\hat{H}} = (\hat{H} \otimes \hat{1} - \hat{1} \otimes \hat{H}^\top) = \frac{1}{2} \begin{pmatrix} 0 & -\varepsilon & \varepsilon & 0 \\ -\varepsilon & 2(\omega + d) & 0 & \varepsilon \\ \varepsilon & 0 & -2(\omega + d) & -\varepsilon \\ 0 & \varepsilon & -\varepsilon & 0 \end{pmatrix}. \quad (\text{F.4})$$

The initial density matrix $\rho_{(0)}$ and its row-wise flattened vector $\sigma_{(0)}$ in Liouville space are:

$$\rho_{(0)} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \Leftrightarrow \sigma_{(0)} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \quad (\text{F.5})$$

Considering singlet-triplet dephasing $\hat{\hat{W}}$,

$$\hat{\hat{W}} = r(\hat{P}^S \otimes \hat{P}^{T+} + \hat{P}^{T+} \otimes \hat{P}^S) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & r & 0 & 0 \\ 0 & 0 & r & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (\text{F.6})$$

gives the Liouvillian superoperator $\hat{\hat{L}} = i\hat{\hat{H}} + \hat{\hat{W}}$. The dynamical equation for $\sigma_{(t)}$ is

$$\frac{d\sigma_{(t)}}{dt} = -\hat{\hat{L}}\sigma_{(t)}. \quad (\text{F.7})$$

Conducting the analogous mathematical process as in equations (5.45-5.47) gives

$$\frac{dp_{(t)}}{dt} = -\hat{\hat{K}}p_{(t)} \Rightarrow p_{(t)} = e^{-\hat{\hat{K}}t}p_{(0)}, \quad (\text{F.8})$$

where

$$p = \begin{pmatrix} \rho_{ST+} + \rho_{T+S} \\ -i(\rho_{ST+} - \rho_{T+S}) \\ \rho_{SS} - \rho_{T+T+} \end{pmatrix}, \quad (\text{F.9})$$

$$\hat{\mathcal{K}} = \hat{\mathcal{M}} + \hat{\mathcal{Q}}; \quad \hat{\mathcal{M}} = \begin{pmatrix} r & -(\omega + d) & 0 \\ (\omega + d) & r & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{\mathcal{Q}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\varepsilon \\ 0 & \varepsilon & 0 \end{pmatrix}. \quad (\text{F.10})$$

The eigenvalues of $\hat{\mathcal{M}}$ are:

$$v_1^{(0)} = 0, \quad v_2^{(0)} = r - i(\omega + d), \quad v_3^{(0)} = r + i(\omega + d). \quad (\text{F.11})$$

The corresponding eigenvectors are the columns of the matrix:

$$V^{(0)} = \begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 1 & 0 & 0 \end{pmatrix}. \quad (\text{F.12})$$

Treating $\hat{\mathcal{Q}}$ as a perturbation to $\hat{\mathcal{M}}$ in the assumption that $\varepsilon^2 \ll ((\omega + d)^2 + r^2)$ and applying the non-Hermitian perturbation theory in Appendix C give the eigenvalues to second order:

$$\begin{aligned} v_1' &= v_1^{(0)} + v_1^{(2)} = r\Omega_z^2, \\ v_2' &= v_2^{(0)} + v_2^{(2)} = (r - i(\omega + d)) - \frac{\Omega_z^2}{2}(r + i(\omega + d)), \\ v_3' &= v_3^{(0)} + v_3^{(2)} = (r + i(\omega + d)) - \frac{\Omega_z^2}{2}(r - i(\omega + d)), \end{aligned} \quad (\text{F.13})$$

and the eigenvectors to first order:

$$V' = V^{(0)} + V^{(1)} = \begin{pmatrix} \frac{\omega\Omega_z^2}{\varepsilon} & \frac{-i}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{r\Omega_z^2}{\varepsilon} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 1 & \frac{\Omega_z^2(r + i(\omega + d))}{\sqrt{2}\varepsilon} & \frac{\Omega_z^2(r - i(\omega + d))}{\sqrt{2}\varepsilon} \end{pmatrix}, \quad (\text{F.14})$$

where $\Omega_z^2 = \varepsilon^2 / ((\omega + d)^2 + r^2) \ll 1$. Thus, using equation (B.8) gives

$$p(t) \approx V' e^{-\Lambda t} V'^{\dagger} p_{(0)} \quad (\text{F.15})$$

where Λ is the diagonal matrix with the three diagonal elements are v_1' , v_2' and v_3' in equation (F.13). Therefore,

$$\begin{aligned} p_3(t) &= \rho_{\text{SS}}(t) - \rho_{\text{T}+\text{T}+}(t) \\ &= \frac{1}{1 + \Omega_z^2} e^{-\Omega_z^2 r t} + \frac{\Omega_z^2}{1 + \Omega_z^2} \cos\left((1 + \frac{1}{2}\Omega_z^2)(\omega + d)t\right) e^{-(1 - \frac{1}{2}\Omega_z^2)r t}, \end{aligned} \quad (\text{F.16})$$

where we have scaled the population difference so that $p_{3(0)} = \rho_{\text{SS}(0)} - \rho_{\text{T}_+\text{T}_+(0)} = 1$. The first term is the low-amplitude oscillatory term decaying fast with a rate constant close to the dephasing rate constant (i.e. $(1 - \Omega_z^2/2)r \approx r$) and the second term is the long-term decaying $1/(1 + \Omega_z^2)$ with a rate constant $\Omega_z^2 r$ can be seen. Taking $\omega = 50 \mu\text{T}$, $d = -200 \mu\text{T}$, $\varepsilon = 20 \mu\text{T}$ and $r = 10^7 \text{ s}^{-1}$, then $\Omega_z^2 r = 1.55 \times 10^5 \text{ s}^{-1}$, much slower than the radical-pair reactions $\sim 10^6 \text{ s}^{-1}$. The time-dependent singlet probability (purple traces in Figure B.1) is obtained remembering $\rho_{\text{SS}(t)} + \rho_{\text{T}_+\text{T}_+(t)} = 1$,

$$\rho_{\text{SS}(t)}^z = \frac{1}{2} + \frac{1}{2(1 + \Omega_z^2)} e^{-\Omega_z^2 r t} + \frac{\Omega_z^2}{2(1 + \Omega_z^2)} \cos\left(\left(1 + \frac{1}{2}\Omega_z^2\right)(\omega + d)t\right) e^{-(1 - \frac{1}{2}\Omega_z^2)r t}. \quad (\text{F.17})$$

Using the symmetric reaction approximation, the singlet yield under a weak magnetic field along the z -axis is obtained,

$$\begin{aligned} \Phi_{\text{S}}^z &= k \int_0^\infty \rho_{\text{SS}(t')}^z e^{-kt'} dt' \\ &= \frac{1}{2} + \frac{k}{2(1 + \Omega_z^2)(\Omega_z^2 r + k)} + \\ &\quad \frac{k \Omega_z^2 \left((1 - \frac{1}{2}\Omega_z^2)r + k\right)}{2(1 + \Omega_z^2) \left(\left((1 - \frac{1}{2}\Omega_z^2)r + k\right)^2 + (1 + \frac{1}{2}\Omega_z^2)^2(\omega + d)^2\right)}, \end{aligned} \quad (\text{F.18})$$

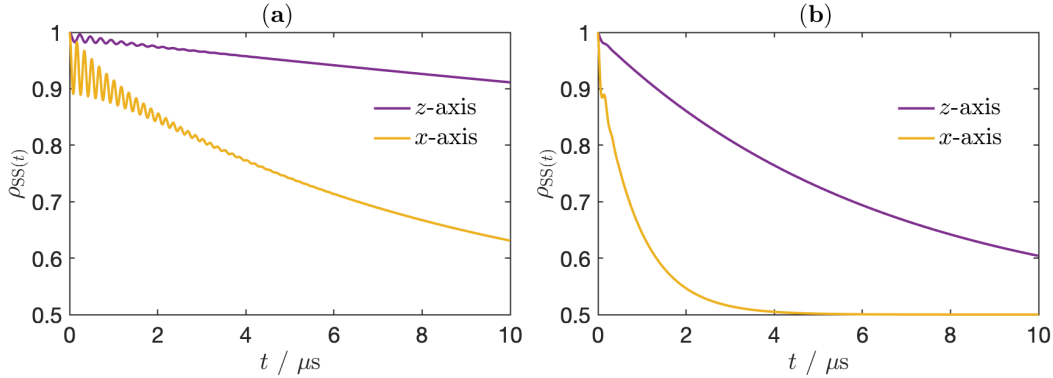


Figure F.1: Two-level S-T₊ system in the nearly degenerate spin subspace with $\omega = 50 \mu\text{T}$, $d = -200 \mu\text{T}$ and $\varepsilon = 20 \mu\text{T}$. (a) for $r = 10^6 \text{ s}^{-1}$ and (b) for $r = 10^7 \text{ s}^{-1}$ illustrate the time-dependent singlet probability, according to equations (F.17) for the weak field along the z -axis and (F.22) for the weak field along the x -axis.

where the second and third terms are attributed to the long-term decay term with the rate constant $\Omega_z^2 r$ and the oscillatory term in equation (F.17) respectively.

Weak magnetic field along the x -axis

The weak magnetic field along the x -axis is represented as,

$$\hat{H}_1^x = \begin{pmatrix} 0 & \omega/2 \\ \omega/2 & 0 \end{pmatrix}. \quad (\text{F.19})$$

The total Hamiltonian is $\hat{H} = \hat{H}_0 + \hat{H}_1^x$, and the commutation superoperator of $\hat{H}$ has the matrix form

$$\hat{\hat{H}} = \frac{1}{2} \begin{pmatrix} 0 & -(\varepsilon + \omega) & (\varepsilon + \omega) & 0 \\ -(\varepsilon + \omega) & 2d & 0 & (\varepsilon + \omega) \\ (\varepsilon + \omega) & 0 & -2d & -(\varepsilon + \omega) \\ 0 & (\varepsilon + \omega) & -(\varepsilon + \omega) & 0 \end{pmatrix}. \quad (\text{F.20})$$

Following similar perturbation treatment through equations (F.5 - F.18) gives

$$\rho_{\text{SS}(t)} - \rho_{\text{T}_+\text{T}_+(t)} = \frac{1}{1 + \Omega_x^2} e^{-\Omega_x^2 r t} + \frac{\Omega_x^2}{1 + \Omega_x^2} \cos\left(d\left(1 + \frac{1}{2}\Omega_x^2\right)t\right) e^{-(1 - \frac{1}{2}\Omega_x^2)r t}, \quad (\text{F.21})$$

where $\Omega_x^2 = (\varepsilon + \omega)^2 / (d^2 + r^2)$. Thus the time-dependent singlet probability under a weak magnetic field along the x -axis (orange traces in Figure F.1) is obtained remembering $\rho_{\text{SS}(t)} + \rho_{\text{T}_+\text{T}_+(t)} = 1$,

$$\rho_{\text{SS}(t)}^x = \frac{1}{2} + \frac{1}{2(1 + \Omega_x^2)} e^{-\Omega_x^2 r t} + \frac{\Omega_x^2}{2(1 + \Omega_x^2)} \cos\left(d\left(1 + \frac{1}{2}\Omega_x^2\right)t\right) e^{-(1 - \frac{1}{2}\Omega_x^2)r t}. \quad (\text{F.22})$$

Then, the singlet yield is

$$\begin{aligned} \Phi_{\text{S}}^x &= k \int_0^\infty \rho_{\text{SS}(t')}^x e^{-kt'} dt' \\ &= \frac{1}{2} + \frac{k}{2(1 + \Omega_x^2)(\Omega_x^2 r + k)} + \\ &\quad \frac{k \Omega_x^2 \left((1 - \frac{1}{2}\Omega_x^2)r + k\right)}{2(1 + \Omega_x^2) \left(\left((1 - \frac{1}{2}\Omega_x^2)r + k\right)^2 + (1 + \frac{1}{2}\Omega_x^2)^2 d^2\right)}. \end{aligned} \quad (\text{F.23})$$

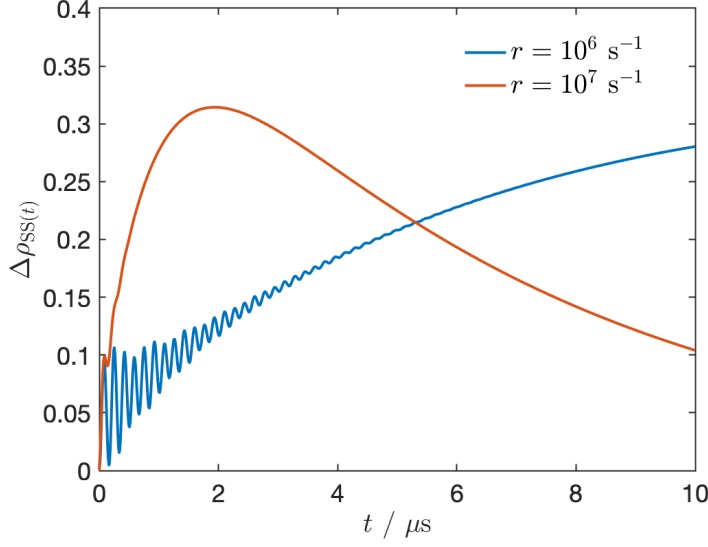


Figure F.2: Two-level S-T₊ system in the nearly degenerate spin subspace with $\omega = 50 \mu\text{T}$, $d = -200 \mu\text{T}$ and $\varepsilon = 20 \mu\text{T}$. $\Delta\rho_{\text{SS}(t)}$ is shown for $r = 10^6$ and 10^7 s^{-1} .

Enhancement of $\Delta\Phi_{\text{S}}$

The anisotropic effect of singlet-triplet dephasing, with respect to the direction of the external field, on the spin dynamics is illustrated in Figure F.2 by calculating $\Delta\rho_{\text{SS}(t)} = \rho_{\text{SS}(t)}^z - \rho_{\text{SS}(t)}^x$. Clearly in Figure F.2, $\Delta\rho_{\text{SS}(t)}$ with $r = 10^7 \text{ s}^{-1}$ is larger than with $r = 10^6 \text{ s}^{-1}$ during $t < 5 \mu\text{s}$ which has covered the radical-pair lifetime. For this simple two-level system, $\Delta\Phi_{\text{S}} = \max_{\theta, \phi}(\Phi_{\text{S}}) - \min_{\theta, \phi}(\Phi_{\text{S}})$, which is used to quantify the directional sensitivity of the magnetic field, is equivalent to

$$\Delta\Phi_{\text{S}} = \Phi_{\text{S}}^z - \Phi_{\text{S}}^x = \int_0^\infty k \Delta\rho_{\text{SS}(t')} e^{-kt'} dt'. \quad (\text{F.24})$$

Here, $\Delta\Phi_{\text{S}}$ is expected to increase when singlet-triplet dephasing rate constant rises from 10^6 s^{-1} to 10^7 s^{-1} (Figure F.2). This is because the second-order perturbation induced long-term decay rate constant, $\Omega^2 r$, varies with respect to the direction of the weak magnetic field and the increase of the singlet-dephasing rate constant can enlarge the difference in $\Omega^2 r$ among magnetic field directions. Calculation of $\Delta\Phi_{\text{S}}$ as a function of r , ranging 10^3 - 10^{10} s^{-1} , for three values of d (0, -100 and $-200 \mu\text{T}$) is shown in Figure F.3(a), which is based on the exact

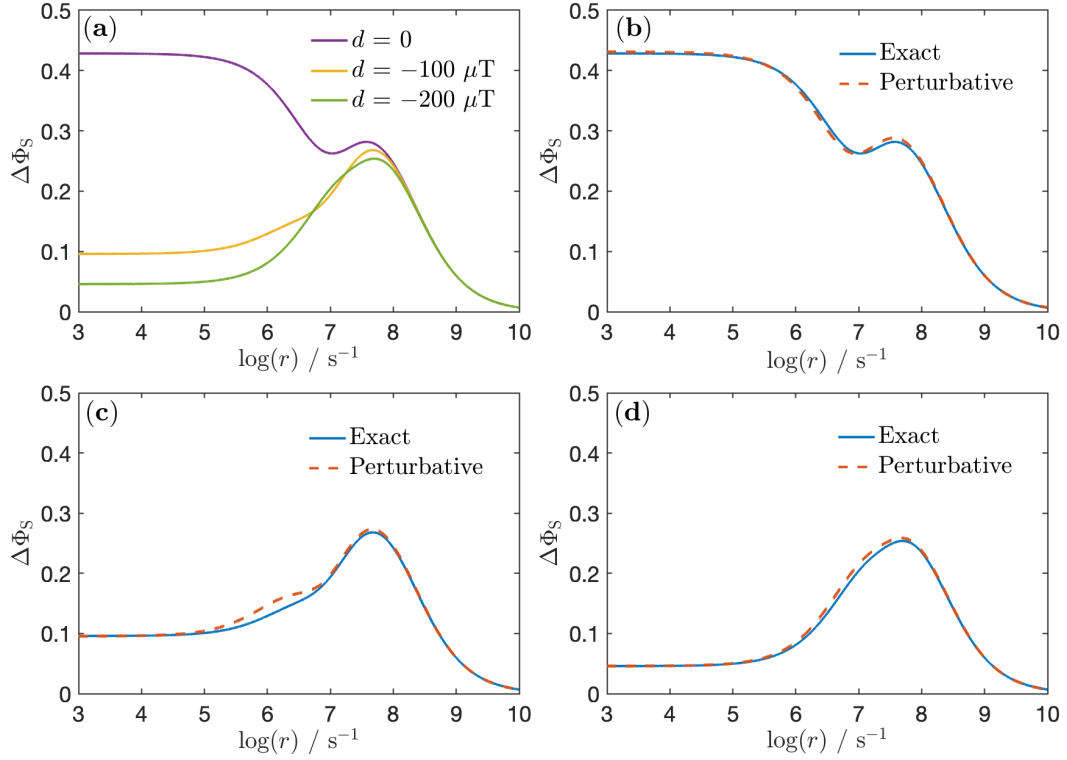


Figure F.3: (a) $\Delta\Phi_S$ as a function of singlet-triplet dephasing rate constant r for three values of d (0, -100 and -200 μT) according to equation (B.7). (b), (c) and (d) Comparison with the perturbation approach.

dynamical equation (F.7) for $\sigma_{(t)}$. The enhancement of $\Delta\Phi_S$ can clearly be seen with r at the order of 10^7 s^{-1} . Assuming that the oscillatory components in equations (F.17) and (F.22) are averaged out by integral over time gives

$$\Phi_S^{z(x)} \approx \frac{1}{2} + \frac{k}{2(1 + \Omega_{z(x)}^2)(\Omega_{z(x)}^2 r + k)}, \quad (\text{F.25})$$

which only preserves the long-term decay contribution. Then, $\Delta\Phi_S$ from the perturbation treatment is obtained as

$$\Delta\Phi_S = \Phi_S^z - \Phi_S^x = \frac{k}{2} \left(\frac{1}{(1 + \Omega_z^2)(\Omega_z^2 r + k)} - \frac{1}{(1 + \Omega_x^2)(\Omega_x^2 r + k)} \right), \quad (\text{F.26})$$

which satisfactorily matches the exact calculation (Figure F.3(b), (c) and (d)). This again proves that the enhancement arises from the anisotropic long-term decay of the population difference between the singlet and triplet states induced by singlet-triplet dephasing.

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