Quantum Mechanical Navigation: The Avian Compass

Holly Herbert
Junior Sophister
Physics

The mechanism enabling the seasonal movement of birds between breeding and wintering grounds defies understanding. It is known that birds derive directional information from the stars, the Sun, and the topographical features which define the planet. Additionally it has been hypothesised that birds may navigate by virtue of ''sensing'' the magnetic field of the Earth. A chemical compass based on the radical pair mechanism has been proposed, and proven viable. Such a quantum mechanical model acts to explain the experimentally determined features of the avian compass and offers a mechanism which is viable in the context of biological systems. This does not imply however that the model is complete. The involved magnetoreceptor molecules remain unidentified, although the protein cryptochrome located in the eyes of birds does hold much promise. In addition, the manner in which the mechanism interfaces with the visual transduction pathway has yet to be understood. Magnetoreception is thus predicted to function in conjunction with other senses in order to facilitate avian navigation.

Introduction

The idea that birds utilise the geomagnetic field of the Earth as a source of directional information was hypothesised as early as 1859 by von Middendorf. The use of a magnetoreceptive compass was first demonstrated in the European robin and thereafter in 17 species of bird (Wiltschko *et al*., 1966). Despite growing evidence that magnetoreception plays a major role in enabling avian navigation, the biophysical mechanism behind such a compass remains elusive.

Any theoretical model must act to explain the experimentally determined features of the avian compass. Wiltschko *et al.* (1972) demonstrated that the employed compass is inclination based, i.e. it is sensitive to the axis but not the polarity of an external magnetic field. Wiltschko *et al.* (1993, 1999) demonstrated that the ability of a bird to orient itself is dependent on the ambient light conditions. European robins showed good orientation under green and blue light, but were disorientated under red. This suggests that the involved mechanism is photo-dependent. Finally, the mechanism responsible for the avian compass must be sensitive to very weak magnetic fields, as that of the Earth is of strength 50μT.

In an attempt to explain all such features, Schulten *et al.* (1978) first proposed a chemical compass based on the radical pair mechanism. They postulated that magnetoreception involved light induced biochemical reactions. The product yields of such reactions have been shown (Schulten *et al.*, 1976) to be influenced by an external magnetic field. Ritz *et al.* (2000) suggested that if such reactions were to take place in immobilised radical pairs (RPs) in the eye of a bird, the product yields may depend on the orientation of the birds head with respect to the geomagnetic field of the Earth. Product yield variations could then affect the sensitivity of the bird's vision and grant it a magnetic map of the Earth.

The Radical Pair Mechanism

A radical is any atom or molecule with one or more unpaired valence electrons. All electrons have intrinsic angular momentum or 'spin' (Pauli, 1924), quantised by the quantum number $S = \frac{1}{2}$. The electron may exist in one of two quantum states, dictated by the magnetic quantum number $M_s = \pm 1$, and regarded as spin up and spin down respectively. The spin of an electron can be represented by an angular momentum vector. Figure 1 illustrates such spin up and spin down states, with a magnetic field applied in the *z*-direction. The Uncertainty Principle dictates that no two directional components of the angular momentum of an electron may be known simultaneously. Thus, in knowing the length of the spin vector and its magnitude along the *z*-direction, the x and y components remain unknown. For this reason the spin vector is represented as precessing about the *z*-direction.

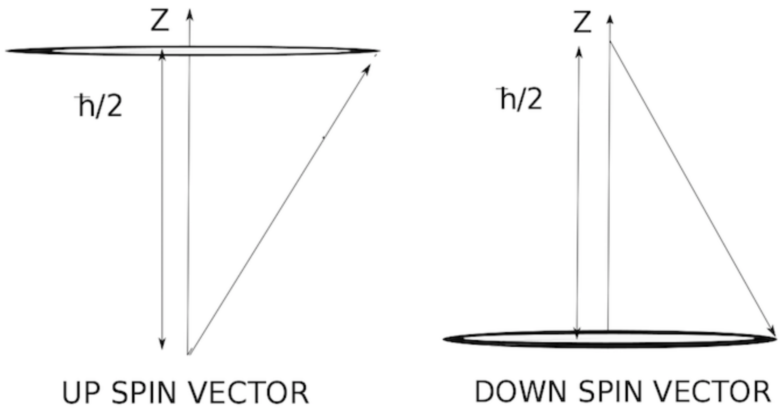

Figure 1. *A vector representation of the spin up and spin down states of the electron.*

A radical pair (RP) may be formed in a spin correlated singlet or triplet state. In the singlet state, the spin vectors of the unpaired valence electrons associated with each radical point in opposite directions. The total spin of the pair sums to zero. In the triplet state, the spin vectors point in the same direction and the net spin is one. Wigner (1927) first introduced the concept of spin conservation in elementary chemical reactions. Spin conservation has been proved (Guo *et al.*, 2011) to be at play in chemical reactions such as electron transfer and bond cleavage and features as the key assumption (Tiersch *et al.*, 2012) in explaining spin chemical effects. Thus, assuming spin is conserved in RP formation, the state in which the RP is generated will match the state of the precursor molecules. A simple radical pair reaction scheme was outlined by Rodgers in 2009 and may be understood in a number of simple steps. The involved magnetoreceptor molecules have yet to be identified and will be referred to as precursor molecules A (acceptor) and D (donor) for the purpose of this review.

Ground state precursor molecules A and D exist in either a singlet ($S=0$) or triplet ($S=1$) state. The photo-excitation of molecule D results in the transfer of a single electron to molecule A and the creation of a radical pair (RP). Each radical possesses one unpaired electron, and the pair is formed in either a singlet or triplet state, matching that of the precursor molecules.

Singlet and triplet radical pairs (RPs) are chemically different and react to produce different products with different reaction rates. Singlet RPs undergo spin-selective reactions to produce singlet products, with reaction rate K_s. The coherent evolution of the spin state of the RP competes with such reactions, and acts to interconvert singlet and triplet RPs. This singlet to triplet interconversion is driven by magnetic interactions within the RP and with an external magnetic field. Triplet RPs undergo their own spin-selective reactions to produce triplet products with reaction rate K_T. The key feature of the radical pair mechanism in the context of magnetoreception is the singlet to triplet interconversion (Rodgers, 2009). An externally applied magnetic field has been shown (Schulten *et al.*, 1976), to effect the singlet and triplet product yields by altering the rate of singlet to triplet interconversion.

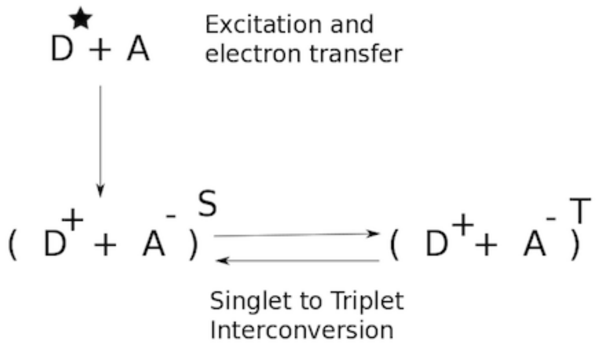

Figure 2. *Adapted from Ritz et al., 2000) A schematic representation of the radical pair mechanism, illustrating radical pair formation and singlet to triplet interconversion.*

Magnetic Field Effects

The manner in which an external magnetic field as weak as 50 μT may affect the spin evolution of a radical pair is one of the key features of the proposed chemical compass. Figure 3 provides a vector representation of the singlet and triplet states of a radical pair. For the purposes of this review, the respective radical spin vectors will be referred to as $\vec{S}_1$ and $\vec{S}_2$. In the presence of an external magnetic field $\vec{B}$, $\vec{S}_1$ and $\vec{S}_2$ precess about the *z*-component of the field at the Larmor frequency (Larmor, 1987).

$$\omega = g\mu_B B \tag{1}$$

ω is the Larmor frequency, μB is the Bohr magneton, B is the magnitude of the magnetic field and g is the electron spin g factor. This is a dimensionless quantity

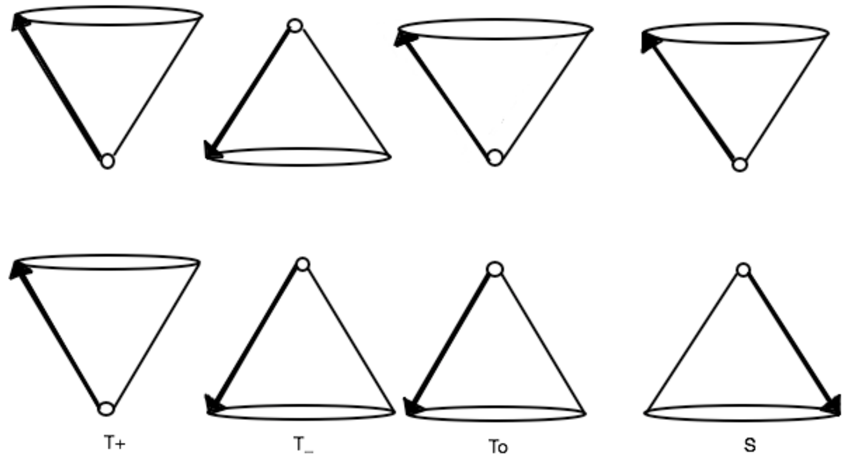

Figure 3. *(Adapted from Steiner, 2007) A vector representation of the radical pair spin states, illustrating the triplet states T_+, T_0, T_- and the singlet state S.*

The singlet state of the radical pair is understood to be the state in which $\vec{S}_1$ and $\vec{S}_2$ precess 180 degrees out of phase and point in opposite directions such that the state has a net spin of zero. With respect to the triplet state, the Zeeman effect lifts the three-fold degeneracy (Zeeman, 1897), and the spin vectors are quantised along the *z*-component of the magnetic field with spin quantum numbers $M_S = -1, 0, 1$ (T_-, T_0, T_+). The associated energy of interaction, ΔE, is given by

$$\Delta E = g\mu_B M_s B \tag{2}$$

The triplet states T_+ and T_- are understood to be the states in which $\vec{S}_1$ and $\vec{S}_2$ are coplanar and precess in phase. The Zeeman interaction shifts both states away from state T_0, with state T_+ increasing in energy and T_- decreasing in energy. State T_0 remains unshifted and so degenerate with the singlet state. The *z*-components of the spin vectors sum to zero, however a resultant spin vector of unit length in the *xy* plane exists, illustrated by noticing that the *x* and *y* components in Figure 4(a) do not sum to zero.

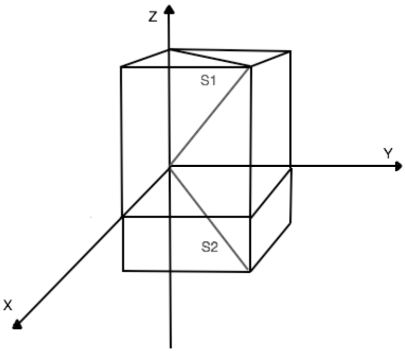

Figure 4a. *Illustation of the triplet state* T_0. *The z-components of the spin vectors may cancel, yet a spin vector of unit length in the xy plane may exist.*

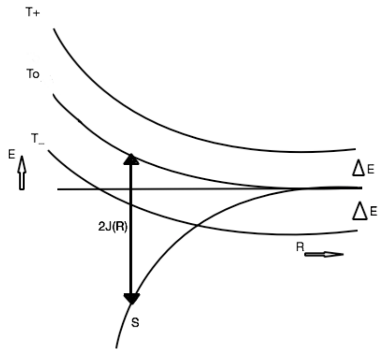

Figure 4b. *(Adapted from Valko, 1988) Illustration of the exchange energy as a function of radical pair separation.*

In order to assess the manner in which an external field may effect the radical pair (RP) mechanism, it is first assumed that the spin correlated valence electrons do not interact. The exchange interaction between two unpaired electrons, if included, would lift the degeneracy of the *S* and T_0 states, separating them by a large energy gap and thus inhibiting any singlet to triplet interconversion. The strength of this interaction falls off exponentially with increasing RP separation, as illustrated in Figure 4(b). The following model, in neglecting this effect, assumes that the RPs are appropriately separated such that interconversion may be facilitated and the exchange interaction may be neglected.

In the context of investigating weak field effects (50 μT), the spin coherent evolution of a radical pair (RP) occurs by virtue of the hyperfine mechanism (Brocklehurst *et al.*, 1995). Hyperfine coupling is an interaction between an electrons total angular momentum $\vec{J}$ and the nuclear spin $\vec{I}$ whereby the nuclear magnetic moment generates a local magnetic field. In the absence of an external field, spin vectors $\vec{S}_1$ and $\vec{S}_2$ precess about the *z*-component of this effective hyperfine field at the Larmor frequency. Each radical may contain several nuclei, and the effective hyperfine field is the vector sum of all individual hyperfine interactions.

It is often the case that the unpaired valence electron associated with each radical experiences a different effective hyperfine field. In this situation, the spin vectors $\vec{S}_1$ and $\vec{S}_2$ precess at different frequencies. Beginning with a singlet-born RP, after time Δt, a phase relationship is reached whereby $\vec{S}_1$ and $\vec{S}_2$ precess in phase. A time $\Delta t'$ later, $\vec{S}_1$ and $\vec{S}_2$ will precess completely out of phase. This process is referred to as spin dephasing, and the oscillation between the singlet state and triplet state T_0 is known as singlet to triplet interconversion, as illustrated in Figure 5(a).

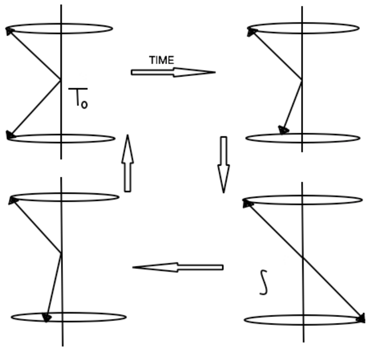

Figure 5a. *(Adapted from Steiner, 2007) Interconversion between the singlet state S and the triplet state* T_0. *Illustrated using the vector spin model in order to highlight the process of spin dephasing.*

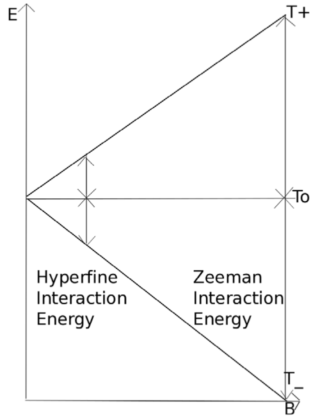

Figure 5b. *Zeeman splitting of the triplet states as a function of magnetic field strength. The extent of the energy shift experienced by states* T_+ *and* T_- *increases with increasing magnetic field.*

In the presence of a weak external field (strength less than that of the hyperfine field), the radical pair spin vectors $\vec{S}_1$ and $\vec{S}_2$ precess about the vector sum of the external and hyperfine field. The Zeeman effects lifts the degeneracy of the triplet states, shifting T_+ and T_- away from T_0. Provided that the interaction energy associated with hyperfine coupling is greater than that associated with the Zeeman effect, interconversion between the singlet state and all three triplet states is facilitated. As a consequence, singlet to triplet interconversion is enhanced and the triplet yield is maximised.

It should be noted that the interconversion between S and $T_{\pm}$ requires a simultaneous flip of the nuclear and electron spins. In order for this to occur, a magnetic field in the *xy* plane must act on the electron spin vector. Hyperfine interactions with surrounding nuclei often provide the necessary torque for such a spin flip. Additionally it should be noted that if both unpaired electrons experienced exactly the same local magnetic fields, no interconversion would be possible.

In addition, the spin coherent evolution of a radical pair may be effected by the Δg mechanism (Boxer *et al.*, 1982). The Δg mechanism enables interconversion between the singlet state and triplet state T_0 only. This mechanism relies on differences in g factors between the spin correlated valence electrons. Differences in g factor result in different precessional frequencies of the spin vectors $\vec{S}_1$ and $\vec{S}_2$ and thus facilitate spin dephasing. Differences in g factor are generally small (typically one part in

10^3 or 10^4 in organic free radicals (Brocklehurst, 1995)) and so strong magnetic fields are required for this mechanism to have a noticeable effect. As a result of the strong field requirement, the interaction energy associated with the Zeeman effect will be larger than that associated with hyperfine coupling, and interconversion between the singlet state and $T_\pm$ is inhibited. Strong fields thus act to minimise the triplet yield. Since this mechanism is known to dominate in large magnetic fields, the effects may be neglected in a model for the avian compass.

In order to describe the state of the radical pairs a spin Hamiltonian is constructed, assuming that the spatial and spin components of the radical pair wave function may be decoupled.

$$H_{RP}(\vec{B}) = g\mu_B\vec{B}\cdot(\vec{S}_1+\vec{S}_2) + g\mu_B\left(\sum_i^a A_{1i}\vec{I}_1\cdot\vec{S}_1 + \sum_j^b A_{2j}\vec{I}_{2j}\cdot\vec{S}_2\right) \qquad (3)$$

The first two terms account for the Zeeman interaction, and the final two terms for the hyperfine interaction. A_{1i}, A_{2j} are the respective hyperfine coupling tensors, a and b are the numbers of nuclei in each component of the radical pair and $\vec{I}_{1i}$ and $\vec{I}_{2j}$ are the respective nuclear spins of radicals 1 and 2. In weak external fields, the Δg mechanism may be neglected such that a single value for the g factor may be used.

Schulten *et al.* (1976) demonstrated that the radical pair (RP) mechanism is sensitive to the strength of an external magnetic field. However, in order to act as a source of directional information, a significant difference in the effects of an external field on RPs must exist, and have different orientations with respect to the field. Ritz *et al.* (2000) proposed and proved that if the hyperfine coupling tensor is anisotropic, the RP will be sensitive to different alignments of the magnetic field. This is unlikely to occur for solution based reactions, as tumbling tends to average any isotropic responses. It was thus concluded that the involved radicals should be oriented and immobilised. The dependence of the triplet yield on the angle between the z-axis of the RP and the axis of the magnetic field is illustrated in Figure 6(a).

The viability of the radical pair (RP) mechanism model in the context of a biological system must be evaluated. The energy of magnetic interaction per particle involved in the RP mechanism is much smaller than the average thermal energy per particle, K_BT. K_B is the Boltzmann constant of value 1.3806 x 10^{-23} $m^2\,kg\,s^{-2}\,K^{-1}$ and T is the temperature, on average circa 300K in biological systems. This does not imply that the effects of the magnetic field become undetectable, since the spins of the electrons bound to the biomolecules are not coupled strongly to the thermal bath. The lifetime of the RPs also plays an important role. Fast decay rates (>10μs^{-1} (Ritz *et al.*, 2000)) of the RPs will not allow sufficient time for the external field to effect the rate of singlet to triplet interconversion. The sensitivity of the RP mechanism increases as the lifetime of the RP increases, as illustrated by Figure 6(b). Given the significance of the decay rates, the values assumed by decay rates in biological systems must be assessed. Decay rates as slow as 1μs-2μs have been realised in biological systems, as well as proved by Mohtat *et al.* (1998) to allow sufficient time for magnetic field induced singlet to triplet interconversion.

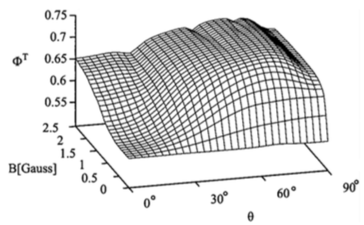

Figure 6a. *(Ritz et al., 2000) The dependence of triplet yield Φ_K on the orientation of the external field with respect to the radical pair is illustrated.*

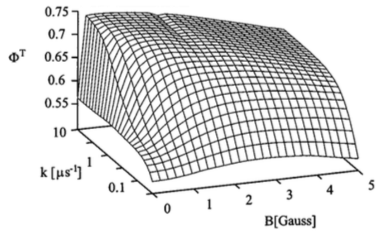

Figure 6b. *(Ritz et al., 2000) The dependence of triplet yield Φ_K on the decay rate k is illustrated.*

Finally, the manner in which the radical pair (RP) mechanism may interact with the visual pathway must be investigated. One suggestion put forth by Ritz *et al.* (2000) is that the RPs may be orientationally fixed on the retina of a bird's eye such that different head orientations of the bird would result in different orientations of the radicals with respect to the magnetic field of the Earth. Different head orientations would thus result in different product yields. Provided that the product yields may affect the sensitivity of light receptors in the eye, this modulation in sensitivity would result in a response pattern that varies over the hemisphere of the eye. A response pattern of light and dark from which the bird may gain directional information would thus be generated. Such a mechanism has been mathematically modelled (Ritz *et al.*, 2000), and could in theory produce a pattern (Figure 7(b)), which may be utilised as a "magnetic map". This suggestion is purely speculative as the manner in which the RP mechanism effects the visual transduction pathway is not yet fully understood.

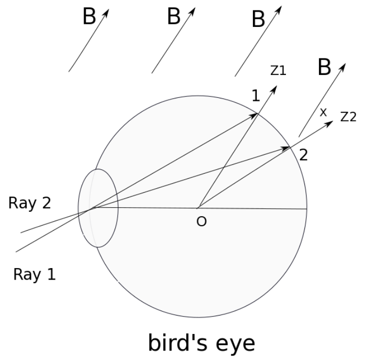

Figure 7a. *(Adapted from Ritz et al. 2000) Illustration of the manner in which radical pairs immobilised on the retina may be influenced by the orientation of the magnetic field of the Earth.*

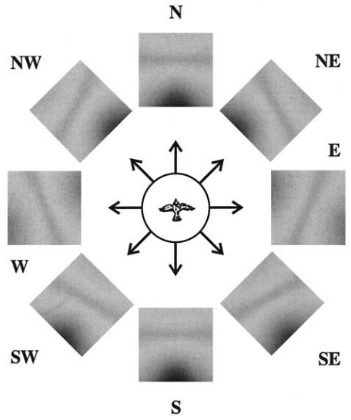

Figure 7b. *(Ritz et al. 2000) Visual representation of the modulation pattern which may be utilised by a bird as a 'magnetic map'.*

Conclusions

The quantum mechanical model of the avian compass has been gaining credibility as evidence mounts in its favour, however the model is by no means complete.

Firstly, the chemicals involved in the radical pair mechanism have yet to be identified, although the protein cryptochrome which has been located in the eyes of several species of migrating bird holds much promise for future research (Solov'yov *et al.*, 2007).

Secondly, the point at which the radical pair mechanism is involved in the visual transduction pathway is not fully understood, and requires more research in the area of Physiology.

Additionally, as an inclination compass is unable to distinguish North from South, the radical pair mechanism alone would not be sufficient to enable navigation. It is likely that the radical pair mechanism is working in conjunction with other senses. For example, the beaks of many birds have been shown to contain the magnetic mineral magnetite, which has been suggested to be linked to magnetoreception (Kirschvink *et al.*, 2001).

While still in its infancy, this model acts to explain many of the experimentally determined features of the avian compass and offers a viable mechanism by which a migrating bird may utilise the geomagnetic field as a source of directional information. A full understanding is within reach and will allow advancements in nanotechnology, as well as offer an insight into how weak magnetic fields influence biological systems, an area of concern in the health industry.

Acknowledgements

The author thanks Mr B. Delaney, Prof. W. Blau and Dr. S. Bergin for helpful appraisals

References

BARNES F.S.B, GREENEBAUM B.G, (2014), 'The Effects of Weak Magnetic Fields on Radical Pairs', Bioelectromagnetics, 2014 Wiley Periodicals, Inc.

BOXER, S.G.B, CHIDSEY C.E.D.C, ROELOFS M.G.R, (1982), 'Use of Large Magnetic Fields To Probe Photoinduced Electron-Transfer Reactions: An Example from Photosynthetic Reaction Centres', *J. Am. Chem*. Soc. 1982, 104

BROCKLEHURST B.B, MCLAUGHLAN K.A.M.L, (1995), 'Free radical mechanism for the effects of environmental electromagnetic fields on biological systems', *International Journal of Radiation Biology*

DEUTSCHLAND M.E.D, PHILLIPS J.B.P, BORLAND C.B, (1999), 'The case for light-dependent magnetic orientation in animals', *The Journal of Experimental Biology* 202, pp. 891-908

EFIMOVA O.E, HORE P.J.H, (2008), 'Role of Exchange and Dipolar interactions in the Radical Pair Model of the Avian Magnetic Compass', *Biophys J* 94

EMLEN S.T.E, (1975), 'Migration: orientation and naviagtion', *Avian Biology*, Volume V, pp.129-291

EVANS E.W.E, DODSON C.D, MAEDA K.M, BISKUP T.B, WEDGE C.J.W, TIMMEL C.R.T, (2013), 'Magnetic field effects in flavoproteins and related systems', The Royal Society publishing, available at: http://rsfs.royalsocietypublishing.org/content/3/5/20130037.short

GOULD I.R.G, TURRO N.J.T, ZIMMT, M.B.Z, (1984), 'Magnetic Field and Magnetic Isotope Effects on the Product of Organic Reactions', *Advances in Physical Organic Chemistry*, 20

GUO D.G, KNIGHT T.E.K, MCCUSKER J.K,M, (2011), 'Angular Momentum Conservation in Dipolar Energy Transfer, Science RE1211459/JEC/CHEMISTRY

KIRSCHVINK J.L.K, WALKER M.M.W, DIEBEL C.D, (2001), 'Magnetite based Magnetoreception' ,Curr. Opin. *Neurobiol*., 11

KRAMER G.K, (1957), 'Experiments on bird orientation and their interpretations', Ibis 99, pp. 196-227

LARMOR J.L, (1897), 'On the theory of the magnetic influence on spectra; and on the radiation from moving ions', *Phil Mag* 1897; Series 5, Vol 44 (271) pp.503-512

MOHTAT N.M, COZENS F.L.C, HANCOCK-CHEN T.H.C, SCAIANO J.C.S, MCLEAN J.M, (1998), 'Magnetic field Effects on the Behaviour of Radicals in Protein and DNA Environments', *Photochemistry and Photobiology*, 67

MOLLER A.M, SAGASSER S.S, WILTSCHKO W.W, SCHIERWATER B.S, (2004), 'Retinal Cryptochrome in migratory passerine bird: a possible transducer for the avian magnetic compass', *Science* 91, pp. 585-588

RITZ T.R, ADE S.A, SCHULTEN K.S, (2000), 'A Model for Photoreceptor-Based Magnetoreception in birds', *Biophysical Journal* 78, pp. 707-718

RITZ T.R, THALAU P.T, PHILLIPS J.B.P, WILTSCHKO W.W, WILTSCHKO R.W, (2004), 'Resonance effects indicate a radical-pair mechanism for avian magnetic compass', *Nature* 429, pp. 177-180

RODGERS C.T.R, HORE P.J.H, (2009), 'Chemical magnetoreception in birds: The radical pair mechanism', *Proc. Natl. Acad. Sci*. USA 106, pp. 353-360

RODGERS C.T.R, (2009), 'Magnetic field effects in chemical systems', Pure Appl. Chem.81

SCHULTEN K.S, STAERK H.S, WELLER A.W, WERNER H.J.W, NICKEL B.N, (1976), 'Magnetic field dependence of the geminate recombination of radical ion pairs in polar solvents', Zeitschrift fur Physikalische Chemie Neue Folge, Bd. 101, pp. 371-390

SCHULTEN K.S, SWENBERG C.E.S, WELLER A.W, (1978), ' A Biomagnetic Sensory Mechanism Based on Magnetic Field Modulated Coherent Electron Spin Motion', Zeitschrift fur Physikalische Chemie Neue Folge, Bd. 111

SOLOV'YOV L.A.S, CHANDLER D.E.C, SCHULTEN K.S, (2007), Magnetic Field Effects in Arabidopsis thaliana Cryptochrome-1, *Biophysical Journal*, 92

STEINER U.S, ULRICH T.U, (1989), 'Magnetic Field Effects in Chemical Kinetics and Related Phenomena', *Chemical Reviews* 89, 1, pp.51-147

TIERSCH M.T, STEINER U.E.S, POPESCU S.P, BRIEGEL H.J.B, (2012), 'Open quantum systems approach to the modelling of spin recombination reactions', *J. Phys. Chem*. A 116\

TIMMEL C.R.T, HENBEST K.B.H, (2004),' A study of spin chemistry in weak magnetic fields', The Royal Society Publishing, Downloaded from http://rsta.royalsocietypublishing.org/ on January 13, 2016

TURRO N.J.T, KRAEUTLER B.K, (1980), 'Magnetic field and Magnetic Isotope Effects in Organic Photochemcial Reactions. A novel Probe of Reaction Mechanisms and a method for Enrichment of magnetic Isotopes', Acc. Chem. Res 1980, 13, pp.369-377

TURRO N.J.T, (1982), 'Influence of nuclear spin on chemical reactions: magnetic isotope and magnetic field effects (A Review)', *Proc. Natl. Acas. Sci*. USA 80, pp. 609-621

TURRO N.J.T, 'Modern Molecular Photochemistry', (1991), University Science Books, pp. 276-282

WILTSCHKO W.W, WILTSCHKO R.W, (1972) , 'Magnetic compass of European robins', Science, New Series, 176, pp.62-64

WILTSCHKO W.W and WILTSCHKO R.W, (1988), 'Magnetic orientation in birds', The *Journal of Experimental Biology* 199, pp. 29-38

WILTSCHKO W.W, MUNRO U.M, FORD H.F, WILTSCHKO R.W, (1993), 'Red light disrupts magnetic orientation of migratory birds', *Nature* (London), pp.525-527

WILTSCHKO W.W, WILTSCHKO R.W, (1999), 'The effect of yellow and blue light on magnetic compass orientation in European robins, Erithacus rubecula', *J. Comp. Physiol*. A

WILTSCHKO W.W and WILTSCHKO R.W, (2005), Magnetic orientation and magnetoreception in birds and other animals, J Comp Physiol A Neuroethol Sens *Neural Behv Physiol*.

WILTSCHKO W.W, TRAUDT A.T, GUNTURKUN O.G, PRIOR H.P, WILTSCHKO R.W, (2002), 'Lateralization of magnetic compass orientation in a migratory bird', *Nature* 419, pp. 467-470

ZEEMAN P.Z, (1897), 'The Effect of Magnetisation on the Nature of Light emitted by a Substance', *Nature* Vol 55

ZHANG Y.Z, BERMAN G.P.B, KAIS S.K, (2015), 'The Radical Pair Mechanism and the Avian Compass: Quantum Coherence and Entanglement', arXiv:1502.00671v2 [physics.bio-ph]

ZHOU Y.Z, (2013), XXlllrd International Congress of Pure and Applied Chemistry, Special Lectures Presented at Boston, USA, 26, 30 July 1971, pp. 22-27

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