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Alan Lewis

Spin Dynamics in Radical Pairs

Doctoral Thesis accepted by
the University of Oxford, UK

 Springer

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Supervisor's Foreword

Organic radical pairs arise in a wide variety of contexts ranging from thin film physics and materials science to chemistry and biology. The Hamiltonians that govern the evolution of the electronic and nuclear spins in these radical pairs, and the equations that allow for the electron spin relaxation and radical pair recombination processes that compete with this coherent spin evolution, have the same form in all of these contexts. The resulting evolution equations are straightforward to write down, and it is also straightforward to derive expressions for all relevant experimental observables. However, these expressions are extremely expensive to evaluate on a computer for all but the smallest of radical pairs, because of the exponential scaling of quantum mechanics with system size. This makes exact quantum mechanical simulations of radical pairs containing more than a handful of hyperfine-coupled nuclear spins totally impractical using standard techniques.

In this thesis, Alan Lewis describes new quantum mechanical methods and semiclassical approximations which can be used to overcome this exponential scaling and make simulations of much larger radical pairs more practical. He then applies these techniques to a variety of problems that arise in disciplines ranging from materials science to biology. An exact quantum mechanical method that exploits the properties of spin coherent states is first applied to the problem of spin-dependent charge recombination along para-phenylene molecular wires, where it is used to extract spin-dependent (singlet and triplet) radical pair recombination rate constants from experimental data. A semiclassical theory based on the precession of classical electronic and nuclear spin vectors is then applied to two separate problems relating to avian magnetoreception: the simulation of a carotenoid-porphyrin-fullerene (CPF) radical pair that has recently been established as a "proof-of-principle" for the operation of a chemical compass, and simulations of the anisotropy of the singlet yield in a flavin-tryptophan radical pair in cryptochrome that has been suggested to play a role in the magnetic compass sense of migratory birds. Finally, a more primitive semiclassical theory due to Schulten and Wolynes is used to simulate the magnetoelectroluminescence and magnetoconductance of both deuterated and undeuterated DOO-PPV organic polymer light emitting diodes. Interesting physical insights are gained in all of these applications,

none of which would have been possible using standard quantum mechanical techniques.

Much of the material presented in the thesis has now been published in scientific papers, including the material in the final chapter on triphasic behaviour in the time-dependent survival probability of the CPF radical pair (A. M. Lewis et al., *J. Chem. Phys.*, 149, 034103, 2018). However, Alan's thesis does contain some details that have not been published elsewhere, including in particular his proof in Sect. 5.1.1 that the radical pair mechanism provides an inclination compass rather than a polarity compass (i.e. that the singlet yield of a radical pair recombination reaction is unchanged on reversing the direction of an applied magnetic field). It is well established from behavioural experiments that migratory birds have an inclination compass, and that this becomes inoperative in the absence of blue-green light. These two facts are among the strongest pieces of circumstantial evidence in favour of the (photochemically induced) radical pair mechanism of avian magnetoreception, so it is nice to see how the inclination compass arises. I am not aware of such a proof having been given before in the literature.

We are now continuing to investigate various aspects of radical pair spin dynamics in Oxford, using both the techniques that Alan describes in his thesis and new techniques that we have developed since he graduated. On the magnetoreception front, we have investigated the sensitivity of the directional information provided by the radical pair mechanism to the presence of weak radiofrequency magnetic fields, and the extent to which this directional information can be used to extract a compass bearing under low light conditions. We have also developed a new quantum mechanical method for studying radicals and radical pairs with very many hyperfine-coupled nuclear spins, and used it to investigate the hyperfine-induced decoherence of electron spins in semiconducting quantum dots. All of this work has been or will soon be published in the open literature.

There are clearly many different physical, chemical and biological problems that one can solve when one knows how to simulate the spin dynamics of radical pairs. We now have the tools to do this for arbitrarily large radicals, thanks in part to the developments described in this thesis. It will be interesting to see how much more can be done with these tools in the future.

Oxford, UK
July 2018

Prof. David Manolopoulos

Abstract

The coherent spin dynamics of radical pairs play a crucial role in their reactions, which consequently cannot be described by a simple kinetic scheme. Instead, simulations of the spin dynamics are required in order to predict the rate and outcome of radical pair reactions, and especially their response to the application of a magnetic field. Unfortunately, the number of spin states of the radical pair increases exponentially with the number of nuclear spins, making deterministic quantum mechanical simulations of realistic radical pairs difficult.

To overcome this difficulty, this thesis begins by presenting an efficient stochastic quantum mechanical method capable of describing a radical pair with as many as 20 nuclear spins, which we use to analyse spin-dependent charge recombination rates along molecular wires. This enables us to identify the mechanism of charge recombination of both the singlet and triplet states of the wire by determining their relative contributions to the overall recombination rate.

We then derive an approximate semiclassical theory which allows to treat the spin dynamics of much larger radical pairs, since the time required for a semiclassical calculation scales linearly with the number of nuclear spins, rather than exponentially. Using this method, we reproduce the results of the first experiments to show that the outcome of a radical pair reaction may be influenced by an Earth-strength magnetic field, and calculate the anisotropy in the singlet recombination yield of the radical pair thought to be responsible for avian magnetoreception.

We show that our semiclassical theory reduces to the earlier Schulten–Wolynes theory under two additional approximations, and use this simpler theory to reveal that singlet-triplet dephasing plays an important role in the spin dynamics of polaron pairs in the semiconducting polymer layer of organic light emitting diodes. We derive a new expression which relates the magnetic field dependence of the electroluminescence and conductance observed in these materials to the singlet yield of the radical pair recombination reaction, which we confirm produces better agreement with experimental data than the relationships used previously.

Parts of this thesis have been published in the following journal articles:

Manolopoulos, D. E. & Hore, P. J. An improved semiclassical theory of radical pair recombination reactions. *Journal of Chemical Physics* **139**, 124106 (2013).

Lewis, A. M., Manolopoulos, D. E. & Hore, P. J. Asymmetric recombination and electron spin relaxation in the semiclassical theory of radical pair reactions. *Journal of Chemical Physics* **141**, 044111 (2014).

Lawrence, J. E., Lewis, A. M., Manolopoulos, D. E. & Hore, P. J. Magneto-electroluminescence in organic light-emitting diodes. *Journal of Chemical Physics* **144**, 214109 (2016).

Lewis, A. M., Fay, T. P. & Manolopoulos, D. E. An efficient quantum mechanical method for radical pair recombination reactions. *Journal of Chemical Physics* **145**, 244101 (2016).

Hiscock, H. G. et al. The quantum needle of the avian magnetic compass. *Proceedings of the National Academy of Sciences of the United States of America* **113**, 201600341 (2016).

Fay, T. P., Lewis, A. M. & Manolopoulos, D. E. Spin-dependent charge recombination along para-phenylene molecular wires. *Journal of Chemical Physics* **147**, 064107 (2017).

Lewis, A. M. et al. On the low magnetic field effect in radical pair reactions. *Journal of Chemical Physics* **149**, 034103 (2018).

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Contents

1	Introduction	1
1.1	Spin	1
1.2	Radical Pair Reactions	3
1.3	Magnetic Field Effects	5
1.3.1	The High Field Effect	5
1.3.2	The Low Field Effect	7
1.3.3	Resonance Effect	9
1.4	Applications	10
1.4.1	Molecular Wires	10
1.4.2	Avian Magnetoreception	11
1.4.3	Magneto-electroluminescence	11
1.5	Outline of Thesis	12
	References	13
2	Quantum Mechanics	19
2.1	The Hamiltonian	19
2.1.1	Exchange Coupling	21
2.1.2	Dipolar Coupling	23
2.1.3	The Zeeman Interaction	24
2.1.4	Hyperfine Interactions	25
2.2	The Recombination Operator	27
2.2.1	The Haberkorn Recombination Operator	27
2.2.2	An Alternative Recombination Operator	28
2.3	Observables	29
2.4	Coherent Spin States	31
2.5	An Efficient Quantum Mechanical Method	33
2.6	Spin Correlation Tensors	37

2.7	Relaxation	39
2.7.1	Modulation of Hyperfine Tensors	39
2.7.2	Singlet-Triplet Dephasing	40
2.8	Conclusion	41
	References	42
3	Semiclassical Approximations	45
3.1	The Semiclassical Theory	46
3.2	Schulten–Wolynes Theory	52
3.3	Comparison of Methods	55
3.3.1	A Simple Radical Pair	55
3.3.2	Asymmetric Recombination Rates	58
3.3.3	Exchange Coupling	60
3.4	Relaxation	61
3.5	Conclusion	62
	References	63
4	Molecular Wires	65
4.1	Mechanisms of Charge Recombination	66
4.2	Simulation Details	67
4.3	Results	71
4.3.1	Shorter Wires	71
4.3.2	Longer Wires	73
4.4	Discussion	75
4.4.1	Resonance Peak Widths	75
4.4.2	Recombination Mechanisms	76
4.4.3	The Origin of the Background	78
4.5	Conclusions	80
	References	80
5	Avian Magnetoreception	83
5.1	Background	84
5.1.1	The Radical Pair Mechanism	84
5.1.2	Cryptochrome	87
5.1.3	The Magnetite Hypothesis	89
5.2	A Prototypical Magnetoreceptor	90
5.2.1	Simulation Details	91
5.2.2	Results and Discussion	93
5.3	Anisotropy	96
5.3.1	Simplified Cryptochrome Models	97
5.3.2	The Full Cryptochrome Radical Pair	101
5.3.3	A Compass Needle?	103
5.4	Conclusion	104
	References	105

6	Magneto-electroluminescence	109
6.1	The Polaron Pair Mechanism	110
6.2	The Relationship Between MEL and MC	112
6.3	Simulating the Singlet Yield	116
6.3.1	Hyperfine Fields in DOO-PPV	117
6.3.2	Singlet-Triplet Dephasing	120
6.4	Results and Discussion	122
6.5	Conclusion	124
	References	124
7	Conclusions and Further Work	127
7.1	Conclusions	127
7.1.1	Theory	127
7.1.2	Applications	129
7.2	Further Work	131
7.2.1	Triphasic Magnetic Field Effects	131
7.2.2	Relaxation	133
	References	136
	Appendix A: Wavepacket Propagation Techniques	139
	Appendix B: Rotationally Averaged Dipolar Coupling	145
	Appendix C: Generalising the Semiclassical Equations of Motion	147
	Appendix D: Schulten–Wolynes Expressions	151
	Appendix E: The Hyperfine Interactions of the Cryptochrome Radical Pair	153

List of Figures

Fig. 1.1	The relative energies of the singlet and triplet states as a function of the applied field strength B	3
Fig. 1.2	An idealised radical pair recombination reaction	4
Fig. 1.3	An illustration of the low field effect (LFE) and high field effect (HFE) on the singlet yield of a singlet-born radical pair	6
Fig. 1.4	$B_{1/2}$ as predicted by the Weller equation, Eq. (1.7), and extracted from simulations, as a function of the hyperfine field of radical 1	7
Fig. 1.5	A diagram illustrating the justification of Eq. (1.8) using the vector model	8
Fig. 1.6	An illustration of the resonance effect on the singlet yield of a singlet-born radical pair	10
Fig. 2.1	The singlet yield of the model radical pair as a function of the applied magnetic field strength B , averaged over M initial nuclear spin states	34
Fig. 2.2	Histograms of 1000 single wavepacket singlet yields, ϕ_s , of the model radical pair at three different applied magnetic field strengths	36
Fig. 3.1	Comparison of the quantum mechanical and semiclassical singlet and triplet probabilities of a model radical pair	49
Fig. 3.2	Comparison of the quantum mechanical and semiclassical xy components of the spin correlation tensors of the electrons in radicals 1 and 2 of a model radical pair	50
Fig. 3.3	The xx , xy , and zz components of the spin correlation tensor of a radical with $N_1 = 1, 4$, and 16 nuclear spins, and the singlet probability of the corresponding radical pair with $N_2 = 0$, no recombination, and no electron spin coupling	57
Fig. 3.4	The relative CPU time taken by the QM and SC methods as the number of nuclear spins in radical 1 increases	58

Fig. 3.5	The quantum mechanical, semiclassical, and Schulten–Wolynes singlet probabilities for a model radical pair with $N_1 = 12$ and hyperfine coupling constants taken from Table 3.1, for three values of Δk and two different magnetic field strengths	59
Fig. 3.6	The quantum mechanical, semiclassical, and Schulten–Wolynes singlet yield of the same radical pair as Fig. 3.5 for two values of Δk	60
Fig. 3.7	The relative singlet yield of the model radical pair described in Sect. 2.5 as a function of magnetic field strength B	61
Fig. 4.1	A typical charge recombination reaction along a donor-bridge-acceptor molecular wire	67
Fig. 4.2	a The chemical structure of the $\text{PTZ}^{\bullet+}-\text{Ph}_n-\text{PDI}^{\bullet-}$ molecular wires. b The positions of the nuclei corresponding the hyperfine coupling constants of the $\text{PTZ}^{\bullet+}$ radical listed in Table 4.1. c The positions of the nuclei corresponding the hyperfine coupling constants of the $\text{PDI}^{\bullet-}$ radical listed in Table 4.2	68
Fig. 4.3	Five pairs of values of (k_S, k_T) which reproduce the overall recombination lifetime of $\text{PTZ}^{\bullet+}-\text{Ph}_3-\text{PDI}^{\bullet-}$ in the absence of a magnetic field are shown in blue	71
Fig. 4.4	The triplet yield of $\text{PTZ}^{\bullet+}-\text{Ph}_n-\text{PDI}^{\bullet-}$ as a function of the strength of the applied magnetic field, relative to the triplet yield in the absence of a field, for $n = 2$ above and $n = 3$ below.	72
Fig. 4.5	The radical pair yield of $\text{PTZ}^{\bullet+}-\text{Ph}_n-\text{PDI}^{\bullet-}$ as a function of the strength of the applied magnetic field, relative to the radical pair yield in the absence of a field, for $n = 4$ above and $n = 5$ below	74
Fig. 4.6	The full width at half maximum of the simulated resonance peak in the triplet yield of $\text{PTZ}^{\bullet+}-\text{Ph}_3-\text{PDI}^{\bullet-}$ as a function of the triplet recombination rate, k_T	76
Fig. 4.7	The singlet and triplet recombination rate constants k_S and k_T of the $\text{PTZ}^{\bullet+}-\text{Ph}_n-\text{PDI}^{\bullet-}$ radical pair for $n = 2 - 5$ extracted from our simulations, plotted as a function of the radical pair separation in those wires	77
Fig. 4.8	A recombination reaction scheme including the possibility of intersystem crossing accompanying charge recombination . . .	78
Fig. 5.1	The structure of the cryptochrome protein is displayed on the left, with the FAD cofactor and Trp residues displayed in the crystallographic orientation for DmCry and AtCry on the right.	88

Fig. 5.2	The 15 magnetic nuclei in the flavin radical are shown above, with the 12 magnetic nuclei in the tryptophan radical shown below	89
Fig. 5.3	The carotenoid-porphyrin-fullerene triad, along with a diagram showing its photochemistry	91
Fig. 5.4	Upper panel: Computed SC magnetic field effects on the total survival probability of the $C^{\bullet+}PF^{\bullet-}$ radical pair at $B = 39 \mu\text{T}$ and $49 \mu\text{T}$. Lower panel: Experimental changes in the transient absorption signal of the carotenoid radical in $C^{\bullet+}PF^{\bullet-}$ at 113 K caused by these applied magnetic fields	93
Fig. 5.5	Dependence of the simulated magnetic field effect in the survival probability of $C^{\bullet+}PF^{\bullet-}$ at $49 \mu\text{T}$ on the relaxation rate k_R of the electron spin on the carotenoid radical	94
Fig. 5.6	The effect of (artificially) moving the electron spin relaxation from the carotenoid radical to the fullerene radical in the $C^{\bullet+}PF^{\bullet-}$ radical pair, compared to no relaxation at all.	95
Fig. 5.7	Anisotropies in the singlet yields of three simplified cryptochrome models.	99
Fig. 5.8	Magnetic field dependence of the QM and SC $\Delta\alpha \simeq \alpha_z - \alpha_x$ for the 22-spin cryptochrome model	100
Fig. 5.9	The anisotropy in the singlet yield of the full cryptochrome system, including dipolar and exchange coupling between the electron spins, in a $50 \mu\text{T}$ magnetic field.	101
Fig. 5.10	The variation of the singlet yield of the 14-spin cryptochrome model as a function of the orientation of the $50 \mu\text{T}$ applied field for a series of decreasing recombination rates	103
Fig. 6.1	Reaction scheme for polarons	111
Fig. 6.2	The repeat unit of 2,5-dioctyloxy-paraphenylene vinylene (DOO-PPV).	112
Fig. 6.3	A comparison of the experimental magnetic field effect on the electroluminescence and conductance of H-DOO-PPV and D-DOO-PPV	113
Fig. 6.4	Voigt fits to the ODMR signals of H-DOO-PPV and D-DOO-PPV	119
Fig. 6.5	The magnetic field effect on the singlet yield of the polaron pair recombination reaction in both H-DOO-PPV and D-DOO-PPV	121
Fig. 6.6	Comparison of the simulated and experimental magnetic field effect on the singlet yield of H-DOO-PPV and D-DOO-PPV	123

Fig. 7.1	On the left, the magnetic field effect on the experimentally measured absorption of the carotenoid-porphyrin-fullerene radical pair, and on the right the field effect on its simulated survival probability	131
Fig. 7.2	The probability of finding the carotenoid-porphyrin-fullerene radical pair in the $ T_+\rangle$ state and the $ T_0\rangle$ state as a function of time, at a range of applied magnetic field strengths	132
Fig. 7.3	The magnetic field effect on the survival probability of the carotenoid-porphyrin-fullerene radical pair tumbling around the long axis of the carotenoid	134
Fig. 7.4	The singlet probability of the carotenoid-porphyrin-fullerene radical pair tumbling around the long axis of the carotenoid after 1.5 μ s	135
Fig. C.1	Comparison of the quantum mechanical and semiclassical singlet and triplet probabilities of a model radical pair which includes electron spin coupling	149
Fig. E.1	The FAD cofactor found in cryptochrome with the magnetic nuclei labelled	153
Fig. E.2	The Trp _C residue found in cryptochrome with the magnetic nuclei labelled	153

List of Tables

Table 2.1	The hyperfine coupling constants used in the model radical pair	34
Table 3.1	The hyperfine coupling constants used in the model radical pair	56
Table 4.1	The hyperfine coupling constants of the $\text{PTZ}^{\bullet+}$ radical in mT	69
Table 4.2	The hyperfine coupling constants of the $\text{PDI}^{\bullet-}$ radical in mT	69
Table 4.3	Exchange coupling constants and the zero-field recombination lifetimes of the $\text{PTZ}^{\bullet+}$ - Ph_n - $\text{PDI}^{\bullet-}$ molecular wires	70
Table 4.4	The coefficients of the polynomial $k_S = ak_T^2 + bk_T + c$ which defines the (k_S, k_T) parameter space consistent the experimental radical pair lifetime of each molecular wire in the absence of a magnetic field	71
Table 4.5	The singlet and triplet recombination rate constants of the $\text{PTZ}^{\bullet+}$ - Ph_n - $\text{PDI}^{\bullet-}$ molecular wires	73
Table 5.1	The isotropic hyperfine coupling constants of the carotenoid cation radical, calculated using the B3LYP functional and the EPR-II basis set.	92
Table E.1	The hyperfine coupling tensors of the $\text{FAD}^{\bullet-}$ radical in mT, calculated using B3LYP density functional theory and the EPR-II basis set	154
Table E.2	The hyperfine coupling tensors of the $\text{Trp}_C^{\bullet+}$ radical in mT, calculated using B3LYP density functional theory and the EPR-II basis set	155