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Alan Lewis

Spin Dynamics in Radical Pairs

Doctoral Thesis accepted by
the University of Oxford, UK

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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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