A Quantum Needle in a Haystack

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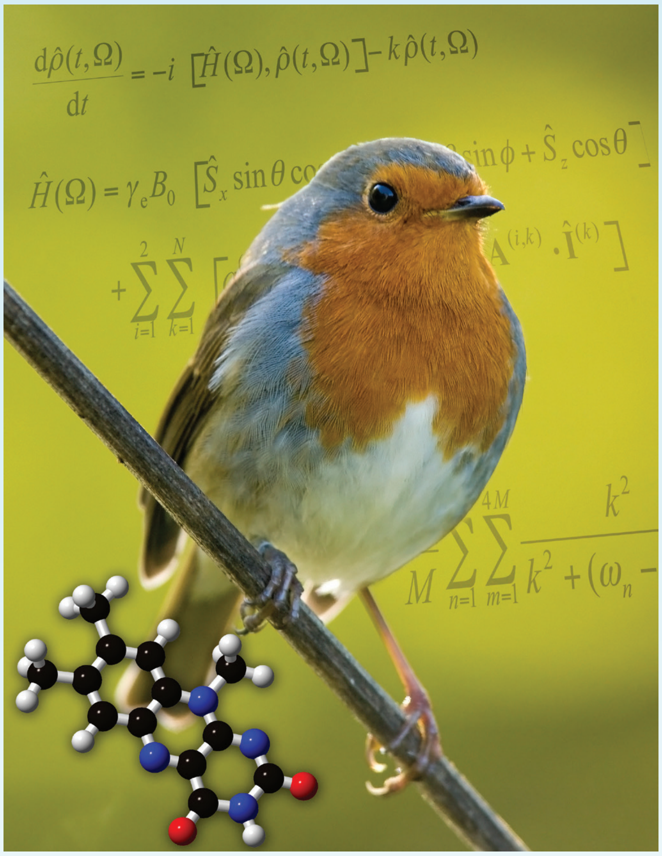
How could a molecular interaction ten million times smaller than $k_B T$ make a significant difference to the yield of a chemical reaction? The answer is not obvious, but it seems likely that migratory birds use such effects to sense the Earth's magnetic field.

It has been known for half a century that birds navigate with the help of a light-dependent magnetic compass, but clues to the mechanism of this extraordinary sense have only emerged in the last ten years. It is thought that birds perceive the geomagnetic field using photochemical reactions in their eyes. The research groups of Christiane Timmel, Stuart Mackenzie and David Manolopoulos in the Chemistry Department, together with my own, are trying to discover whether this is indeed the case and how, in detail, such a sensor could work.

The primary magnetoreceptor is believed to be cryptochrome, a blue-light photoreceptor protein found in a variety of different cell types in the avian retina. Photo-induced electron transfer within the protein produces pairs of radicals in which the unpaired electron spins are correlated and far removed from their equilibrium configuration. As a consequence, and because the radical recombination reactions conserve spin, weak magnetic interactions can affect the yield of a conformation of the protein that could act as a signalling state. Because the spins are not at equilibrium, the interactions can be small compared to $k_B T$ and still have this effect. *

Experimental and theoretical evidence is accumulating in support of this mechanism although much of it remains frustratingly circumstantial. There are many fundamental puzzles, some of which we are attempting to unravel. The Timmel group has done experiments on a molecular triad composed of covalently linked carotenoid, porphyrin, and fullerene molecules to establish the principle that a radical pair can respond to a magnetic field as weak as the Earth's. Using specifically developed spectroscopic techniques, the Timmel and Mackenzie groups have shown that cryptochrome photochemistry is indeed sensitive to weak magnetic fields *in vitro* and that the proteins appear to be fit for purpose as magnetic compass sensors. The Manolopoulos group is developing theoretical methods that allow the spin dynamics of realistic radical pairs, including the aforementioned triad molecule, to be accurately modelled *in silico*.



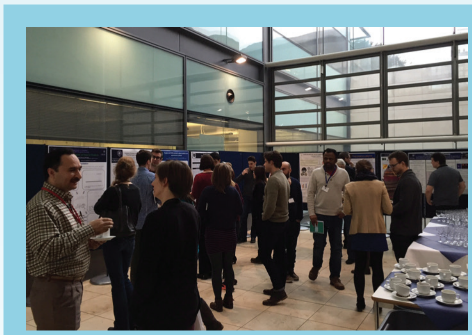
One ongoing project is a collaboration with Henrik Mouritsen, a biologist at the University of Oldenburg in Germany. When tested on the university campus in Oldenburg, migratory European robins are incapable of using their magnetic compass unless they are efficiently shielded from the very weak electromagnetic fields ("electrosmog") generated by electrical equipment in the nearby laboratories. In the countryside, a few miles outside the city, the same birds orient perfectly well. Even though it is clear that radical pair chemistry can be influenced by time-dependent magnetic fields, it is astonishing that such weak electromagnetic noise — at a level below the World Health Organization's recommendations for safe human exposure — could disrupt the behaviour of a higher vertebrate. The challenge is now to determine the origin of the effect using a combination of behavioural studies, laboratory experiments on cryptochromes, and computational modelling. We hope that electrosmog disorientation will provide powerful insights into the inner working of the compass sense.

Other work is supported by the Air Force Office of Scientific Research which is concerned about the American military's over-reliance on global positioning systems. In one project, we have shown that the radical form of the flavin chromophore in cryptochrome has magnetic interactions that could result in the protein being a much better compass than previously thought. The hyperfine interactions in the flavin radical are such that the quantum oscillations of the spin-coherence can be exquisitely sensitive to the direction of the geomagnetic field. All we have to do now is to establish whether the conditions necessary for the realisation of this "quantum needle" are compatible with the warm, wet and noisy environment of a magnetoreceptor cell.

It would be nice to get to the bottom of this least understood of sensory mechanisms, and better still if practical applications emerged along the way. In the last few years it has been found that semiconductors constructed entirely from non-magnetic organic materials exhibit room-temperature changes in their current and light output that can be tuned by weak, externally applied magnetic fields. The spin physics behind these effects is essentially identical to the radical pair mechanism, with polarons playing the role of the radicals. With "bio-inspiration" gleaned from studies of the bird-compass it may be possible to make cheap, electronically addressable magnetic sensors from non-toxic organic materials. As a first step in this direction, the Manolopoulos group has recently made considerable inroads into understanding the detailed relation between magnetoelectroluminescence and magnetoconductance in organic light emitting diodes.

One thing that comes out of all of this is that the disparaging term "bird brain" should more correctly be regarded as a compliment. Birds may not have a SatNav capability but they could well "know" a bit more chemistry (and quantum mechanics) than anyone realized: ChemNav, perhaps?

* See Hore and Mouritsen, *Annu. Rev. Biophys.* 45 (2016) 299–344, in which we attempt to explain the physics and chemistry of radical pair magnetoreception to biologists and the biology and chemistry to physicists. $k_B T$, Boltzmann's constant multiplied by temperature, is the the energy associated with the ever-present random motions of molecules as they bump into one another, rotate, and vibrate.



Launch of ChemBioPlants network

2016 saw the launch of a new network to bring together researchers from the Departments of Chemistry, Biochemistry and Plant Sciences. ChemBioPlants aims to foster and support new collaborations at the interface of these disciplines, providing a forum through which researchers can explore ideas and identify projects where complementary approaches will be advantageous. By combining expertise, such interdisciplinary research will be able to help address issues of global importance such as food security, sustainable agriculture, exploitation of plant natural products, bioenergy and the relationship between food and health.

Two networking events held so far this year have been very successful, with short talks and poster sessions from across the departments revealing the breadth of excellent research going on in Oxford as well as highlighting multiple opportunities to work together. Importantly, the network has been able to provide small grants to kick-start new collaborative projects, all of which are now under way. Further events will take place on a termly basis, and a website is being developed as a portal to access research interests across the network, as well as news, funding opportunities and research success stories.