

IN-DEPTH

The Quantum Robin



Migratory birds navigate with the help of the Earth's magnetic field, but how do their compasses work? Peter Hore of Oxford University discusses whether quantum coherence and entanglement could be the answer.

Writing in 1975, Peter Atkins, a physical chemist at Oxford University, described studies of the effects of magnetic fields on chemical reactions as a 'romping ground for charlatans.' He went on to say: 'Contributions to the literature of the subject range over the span of scientific competence, from the benignly insane to whatever lies at the other extreme removed by a hair's breadth from the first.' This situation has changed over the last 36 years. Today, a number of scientists (who do not appear to be charlatans) believe that the magnetic compass sense of migratory birds could be based on magnetically sensitive chemical reactions in the eye.

Equilibrium and Non-Equilibrium

It has been clear since the 1960s that birds have a compass that responds to the direction of the Earth's magnetic field and helps them navigate during their spectacular annual migrations. However, it is still uncertain how this compass works. If asked whether a magnetic field as weak as the Earth's could influence the chemical transformation of one molecule into another, most scientists would look at you as if you were mad. Their reasoning would go something like this: molecules are perpetually in motion, bumping into one another, rotating and vibrating. The average energy associated with these random motions, often called the thermal energy, is used as a yardstick against which to assess other energies. For example, the chemical bonds that hold atoms together within molecules typically have energies 10–100 times stronger than the thermal energy, which is why molecules generally don't shake themselves to bits. Following the same logic, if you try to influence the chemical behaviour of a molecule by supplying an amount of energy

much smaller than the thermal energy, then nothing much is likely to happen; your tiny disturbance will simply be overwhelmed by the ever-present random motions. This is precisely the situation for magnetic fields. Individual molecules are weakly magnetic and so interact feebly with even the strongest man-made magnetic fields, let alone the Earth's magnetic field which is puny by comparison. This perfectly sensible line of reasoning would appear to rule out the possibility of a magnetic field effect on a chemical transformation. But magnetic fields can and do alter chemical reactivity, by a means that makes the above argument irrelevant, as we shall see.

To get an idea of why minuscule energies can affect chemical reactions, think about the (non-chemical) process shown in Figure 1. Imagine we have a block of granite weighing a kilogram or more and ask whether a fly would be able to tip it over. Common sense says the answer, surely, is no. But suppose I were to poise the stone on one of its edges. Clearly it would not

be stable in such a position and would tend to fall to the left or the right if left to its own devices. Now suppose that while the block is teetering in this way a fly were to land on its right-hand side. Even though the energy imparted by the fly would be tiny, it could be enough to cause the block to fall to the right rather than the left. Thus, tiny energies can have large effects, but only if you first prepare the system (in this case the block of granite) in the right state — far from equilibrium.

Radicals, Spins and Coherence

How can this be translated to the realm of chemistry? First we would need to supply energy to the molecules so as to produce a suitable

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non-equilibrium state. Then it would have to be possible for a tiny magnetic energy to push these specially prepared molecules along a desired reaction pathway. Scientists have known how to do this since the 1970s: the key players in this game are short-lived forms of molecules called *radical pairs*. When a photon of light, for example from the Sun,

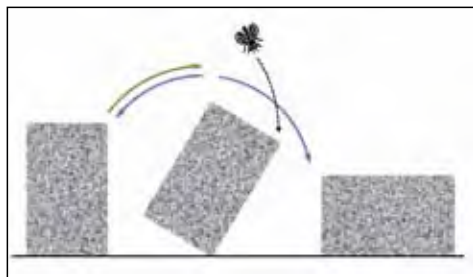


Figure 1. Thinking about how a fly might be able to knock over a block of granite can help one understand how the Earth's magnetic field affects a chemical reaction.

hits a molecule, its energy can be absorbed, causing the molecule to split into fragments called *radicals*. Typically one chemical bond breaks at a time so that the radicals are created in pairs. To understand why radical pairs are so special, we need to think about their magnetism, which stems from the *spin* of their electrons. Spin is a quantum mechanical property of sub-atomic particles and associated with it is a *magnetic moment*; that is, particles with spin are magnetic. Now, atoms are usually held together in molecules by electrons, two to each bond. So when a chemical bond is broken one electron ends up in each of the radicals. Quantum mechanics tells us that there are just two forms of this radical pair: a *singlet* state in which the two magnetic moments are opposed, like this $\uparrow\downarrow$, or a *triplet* state in which they are aligned, like this $\uparrow\uparrow$. Roughly speaking, one can think of the two electrons as a pair of bar magnets which would repel or attract depending on whether they had like-poles facing one another ($\uparrow\uparrow$) or opposite poles facing ($\uparrow\downarrow$). If the two radicals are not too close together then the two spin-states, singlet and triplet, have almost identical energies (like the $\uparrow\uparrow$ and $\uparrow\downarrow$ arrangements of widely separated bar magnets) making it possible to convert one into the other with a tiny input of energy. This situation is analogous to the wobbling granite.

In fact the behaviour of radical pairs is much more interesting than a balancing stone. The radical pairs undergo a complicated dance, oscillating from singlet to triplet and back again several million times per second. This behaviour is purely quantum and is a consequence of the *coherence* of the electron spins. The two spins behave coherently because they were created simultaneously and because there are local magnetic interactions within each of the radicals. As singlet and triplet have essentially identical energies, even the Earth's tiny magnetic field can alter the timing and extent of the dance. This is the equivalent of the fly landing on the stone block.

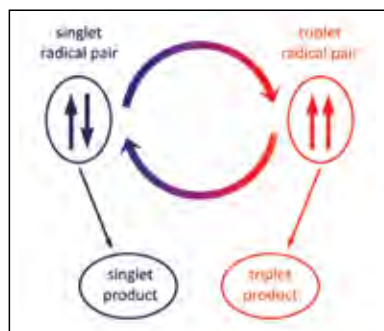


Figure 2. The dance of the radical pairs. If a magnetic field causes a singlet radical pair to whirl faster into a triplet radical pair, fewer molecules of the singlet reaction product will be formed and correspondingly more molecules of the triplet reaction product. If it took place inside a bird's body, this sort of chemistry could form the basis of a magnetic compass.

strength of the kick depends on the orientation of the radical pair, then in principle we have a direction sensor: all the bird needs is a way of registering the change in the amount of one of the chemical reaction products.

Cryptochrome

The possibility that birds' magnetic compasses might be based on a light-induced chemical reaction in the eye was suggested by Klaus Schulten, now at the University of Illinois at Urbana-Champaign, in a far-sighted paper at a time (1978) when the *radical pair mechanism* was in its infancy. Only later did Wolfgang and Roswitha Wiltschko, working at the University of Frankfurt discover that, as Schulten had anticipated, birds need (blue or green) light for their compass to work. In the following 20 years, radical pairs came of age and many chemical processes in which they are involved are now known to be affected by magnetic fields, albeit fields considerably stronger than that of the Earth. This area of science — using magnetic fields to study radical chemistry and physics — has become known as *Spin Chemistry*. Nevertheless, Schulten's suggestion was largely ignored until 2000 when he and Thorsten Ritz at the University of California, Irvine, proposed that the required photochemistry could occur in a protein called *cryptochrome* contained in the bird's retina. Over the last 11 years a substantial body of evidence has accumulated to support the 'cryptochrome hypothesis' (see Miriam Liedvogel's article in *Navigation News* in 2009). However, it is still not certain that this is how the compass works; there are plenty of sceptics who remain to be convinced.

An Unlikely Molecule

One obstacle to accepting the radical pair mechanism of magnetic sensing has been removed by my colleagues in Oxford, Christiane Timmel, Kiminori Maeda and Kevin Henbest and their co-workers. To provide a proof of principle that a chemical compass could be a viable proposition, they chose to study a molecule completely unrelated to cryptochrome (and one that you would not expect to find in a bird's

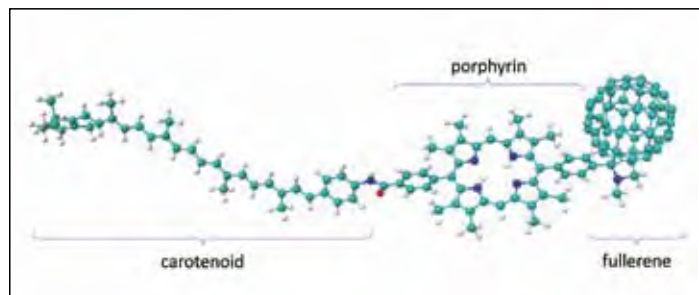


Figure 3. This molecule has been used to demonstrate the principle of a chemical compass. The balls represent atoms: carbon (turquoise), hydrogen (white), oxygen (red), and nitrogen (blue). The sticks linking the balls represent chemical bonds. The magnetically sensitive radical pair is formed by light-induced transfer of an electron from the carotenoid to the fullerene via the porphyrin. The molecule is less than 10 billionths of a metre from end to end.

eye or anywhere else in a living system). As can be seen from Figure 3, this *triad* molecule, which I shall call CPF, is comprised of three linked parts, a *carotenoid* (C), a *porphyrin* (P) and a *fullerene* (F). CPF was made by Devens Gust, a photochemist at the University of Arizona, for a different purpose but it suited the Oxford group well because Gust's work had shown that it undergoes the same sort of photochemical transformations as cryptochrome. What Timmel and her colleagues did was to shine pulses of green laser light lasting less than 10 nanoseconds (10 billionths of a second) onto CPF molecules to form radical pairs and to measure how long they lived. Having first shielded the molecules from the natural magnetic field, they found that these lifetimes, which are about a hundred nanoseconds, changed

when they switched on a magnetic field weaker than that of the Earth. They then went on to demonstrate that the size of the response to a (somewhat stronger) magnetic field depended on its direction, so establishing the feasibility of a chemical compass for use in navigation ('ChemNav', perhaps?).

Entanglement

Returning to the quantum world, it turns out that the electron spins in a radical pair are not only coherent but also have a property known as *entanglement*, a term introduced by Erwin Schrödinger, one of the pioneers of quantum theory, in 1935. Entangled states cannot accurately be described in terms of the properties of their component parts considered separately. In the radical pair context, this means that the behaviour of one electron spin is affected by what happens to the other electron spin even though the radicals may be far apart. Einstein described this sort of thing as 'spooky action at a distance.' Physicists get excited by entanglement because they can do things with entangled states that are impossible with merely coherent states. An example is *quantum computation*: by using entangled quantum bits, or qubits, calculations can be done much more efficiently than with the classical bits in conventional processors. The problem is that entanglement — often described as exotic and fragile — is generally difficult to create and preserve. Usually, entangled states have to be studied under special, carefully controlled conditions (for example, extremely low temperatures and/or high vacuum). Also, the entanglement may only exist fleetingly because, like coherence, it has a tendency to leak away as a result of the 'noise' produced by random molecular motions. This process, known as *decoherence*, can be fast: decoherence times of a few picoseconds (trillionths of a second) are not uncommon. Physicists interested in quantum information processing were therefore excited when they discovered recently what spin-chemists had known for years, that spins in radical pairs are easily entangled at normal temperatures and pressures and can remain so for as long as a microsecond (a millionth of a second). And, even better, it seems that this could be happening in the warm, messy, watery environment of a bird's eye. If Nature has found a way to prolong the lifetime of spin-coherence using biologically available materials and structures, perhaps the same principles could be used to protect man-made quantum devices from the pernicious effects of decoherence. If the bird-compass really does prove to be based on radical pair chemistry, then this will be a clear-cut example of a fundamentally quantum biological process, that simply could not happen by a classical chemical mechanism, as shown by the thermal energy argument. For these reasons, radical pair magnetic sensing finds itself part of the emerging scientific field known as *Quantum Biology*.

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Robins and Radiofrequencies

A key experiment, performed as a diagnostic test for the involvement of radical pairs in magnetic sensing, may shed light on this question of spin-decoherence. Ritz and the Wiltschkos subjected caged robins to time-dependent magnetic fields to see whether their ability to detect the Earth's magnetic field could be disrupted. The idea behind the work came from previous observations that a radical pair's dance can be modified by an oscillating magnetic field at the correct frequency. Just as an operatic soprano can, reputedly, shatter a wine glass by singing at the pitch that matches its natural resonance frequency, so one can interfere with the choreography of a radical pair using a magnetic field of the appropriate frequency. What Ritz and his colleagues found was truly remarkable. When subjected to a radiofrequency magnetic field oscillating at 1.3 MHz (1.3 million cycles per second) some

3,000 times weaker than the natural magnetic field, the birds were no longer able to orient themselves magnetically. At half or at double that frequency, the radiofrequency field had to be 30 times stronger to have a similar disruptive effect on the birds' magnetic compass. If these experiments can be successfully repeated in another laboratory (independent replication is the gold standard in scientific research), these results provide the most convincing evidence so far that the compass is radical pair-based. There are solid physical reasons why radical pairs subject to the Earth's magnetic field in Frankfurt should resonate near 1.3 MHz and why other proposed magnetic sensory mechanisms should not be sensitive to this frequency. The reason the results are so striking is that the radiofrequency magnetic field that produces this resonance is incredibly weak.

There are (at least) two ways to understand the birds' pronounced sensitivity at 1.3 MHz. First, spin-decoherence could be exceedingly slow. It requires time for a radical pair to respond to a magnetic field: the weaker the field, the longer is needed for it to have a significant effect. A decoherence time of a microsecond is long enough for the Earth's field to affect the singlet-triplet dance. A radiofrequency field more than a thousand times weaker would require the decoherence

to be more than a thousand times slower to produce a similar effect. Such a leisurely leakage of electron spin-coherence is unprecedented in many years of laboratory studies of radicals. Microsecond decoherence is relatively routine; a thousand microseconds would require some pretty unusual conditions. This is why radical pair magnetic sensing has intrigued quantum physicists. If this

explanation is correct and the reasons for the slow decoherence can be understood, it may be possible to make much more efficient quantum devices.

The second interpretation is that decoherence is not abnormally slow but that the compass is simply exquisitely susceptible to feeble radiofrequency magnetic fields, perhaps as a by-product of extreme sensitivity to the natural magnetic field. But how could the minuscule effect of the radiofrequency field outweigh the presumably much larger effect of the Earth's magnetic field? This would be like expecting a speck of dust landing on the left-hand side of the block in figure 1 to counteract the fly's ability to cause it to fall to the right. There surely can be no reason why birds would have evolved to be so susceptible to radiofrequency fields which contain no useful directional information and have only been prevalent as a result of human activity over the last 100 years or so. In short, if proved to be correct, either of these interpretations of the Frankfurt results would be astounding and, at the same time, fascinating for the insight it would give into the inner workings of this intriguing sensory mechanism.

About The Author

Peter Hore is in the Department of Chemistry at Oxford University. Some information on what his research group gets up to can be found at <http://research.chem.ox.ac.uk/peter-hore.aspx>.

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