Viewpoint

Vive la Différence!

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Long-lived singlet states—zero-spin states made of two spin-1/2 particles—can be created by combining two different atomic species such as carbon and hydrogen.

Subject Areas: **Magnetism, Chemical Physics**

A Viewpoint on:
Long-Lived Heteronuclear Spin-Singlet States in Liquids at a Zero Magnetic field
M. Emondts, M. P. Ledbetter, S. Pustelny, T. Theis, B. Patton, J. W. Blanchard, M. C. Butler, D. Budker, and A. Pines
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Where would we be without singlet states? Almost all molecules in nature—and in our bodies—exist as singlet states, which arise when two particles with a spin of 1/2 combine into an eigenstate with zero spin. Their most common occurrence is in stable atomic or molecular orbitals. Their combination into a spinless state frees the pair from angular/magnetic momenta, leading to a particularly stable diamagnetic combination. Because they don't have a net magnetic moment, singlets are long-lived states. This is a property with important practical implications for nuclear magnetic resonance (NMR): although singlets are not directly measurable in NMR, their long lifetime can be exploited to enhance the sensitivity of NMR experiments and extend the range of dynamic phenomena that NMR can probe [in either its spectroscopic (NMR) or imaging (MRI) modes].

A *sine qua non* condition for creating such singlet states is that its constituents be identical—or at least so we believed. But now, a study in *Physical Review Letters* by Meike Emondts from RWTH Aachen University, Germany, and co-workers demonstrates a singletlike state made of two different spin-1/2 particles: a hydrogen (^{1}H) nucleus and a bonded carbon-13 (^{13}C) counterpart [1]. Evidence for the singlet nature of the state they construct is given by the long lifetime of this state, which exceeds the lifetime of either atom by a factor of 3. The demonstration of heteronuclear singlets thus challenges theoretical preconceptions and dramatically extends the range of systems that can be potentially probed via enhanced forms of singlet-state-based NMR.

The creation of long-lived singlets has been previously reported for ions and electrons [2] but required complex manipulations. Nuclear spins, which interact more weakly with the environment, can offer a more sheltered "playground" for studying unusual spin states. Singlet nuclear states have, in fact, long been known and manipulated, starting with the discovery of the spin isomer of the H_2 molecule, known as parahydrogen. This isomer can be prepared by cooling H_2 below its characteristic rotational temperature (88 kelvin), and it is characterized by having its two protons in the $(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)/\sqrt{2}$ antisymmetric combination. In this singlet state, the molecule has a total nuclear spin of zero. Although magnetically silent and thus invisible to NMR, parahydrogen can enhance the sensitivity of NMR and *in vivo* MRI. This is due to the fact that the singlet symmetry can be broken via a chemical reaction known as hydrogenation [3], whereby the two hydrogens bond to two inequivalent atoms, converting the pair's perfect (but magnetically silent) antialignment into an effective spin polarization. This, in turn, leads to a pronounced difference in the spin populations of each hydrogen site—a so-called hyperpolarized state—enabling their resulting magnetic fields to be detected by NMR/MRI experiments with a dramatically enhanced sensitivity.

Unfortunately, there are few options for manipulating parahydrogen: other than chemical processes that break its symmetry, there are no ways of "talking" to it. Over the last decade, however, research has demonstrated that one could create an entangled singlet state out of a pair of homonuclear spins that are chemically slightly different [4]. This can be done in a number of ways. The most intuitive option is to apply a series of so-called refocusing magnetic pulses that erase the spins' chemical shifts (i.e., their different precession frequencies in an applied magnetic field). Such a pulse sequence can thus "turn off" the inequivalence of protons in the two different molecules. With proper magnetic manipulations, the pair of spins can be combined to create a singlet state. This long-lived state will be conserved while the pulse sequence is executed, but by stopping the refocusing pulses, it can be later transformed back into an observable that is detectable by NMR.

Now, Emondts *et al.* take this concept a step fur-

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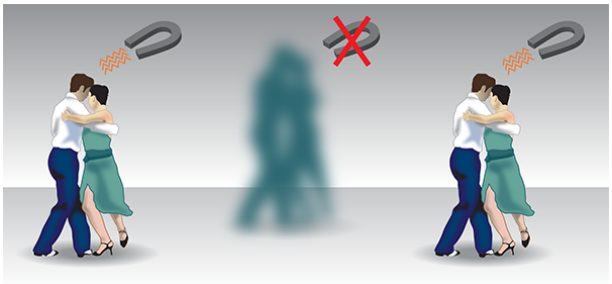

FIG. 1: Clearly distinguishable in most instances, heteronuclear pairs can be driven into a long-lived singlet spin state when $B_o = 0$. (APS/Alan Stonebraker)

ther and demonstrate that such toggling is also feasible when dealing with heteronuclear spins, i.e., pairs composed of nuclei as different as ^{13}C and ^{1}H. Key to generating a "heteronuclear singlet" is erasing the difference between the magnetic couplings that the spins will naturally present when inserted in a magnetic field. These differences will be stronger than in the homonuclear all-^{1}H case. They will not be determined by chemical effects but rather by the different nuclei gyromagnetic ratios of ^{13}C and ^{1}H; i.e., by the isotope-specific constants defining the species' NMR precession frequencies in a magnetic field.

To cut the Gordian Knot presented by this intrinsic nuclear difference, Emondts *et al.*'s solution is as drastic as it is simple: make the magnetic field as close to zero as possible. The authors achieved this by exploiting tricks from zero-field NMR, a "shuttling" based technique first developed in the 1980s [5]. To achieve the heteronuclear singlet state, this meant reducing the difference between the ^{13}C and ^{1}H Larmor frequencies from the usual 10 to 100 megahertz values, to only 3.2 hertz. This difference is much smaller than other interactions to which the spins may be subjected, including the mutual ^{13}C-^{1}H J coupling (a form of spin-spin coupling mediated by the electrons in the molecular bonds connecting the two spins). At zero magnetic field, this J coupling becomes the dominant term in the spin Hamiltonian, and a suitable shuttling of the system will thus make the spin pair evolve into one of its allowed states, one of which is a singletlike state involving the two spins. Hence a paradoxical "heteronuclear singlet" state can be originated (see Fig. 1).

Emondts *et al.* confirmed that they reached this state by dividing their experiment into three phases: (i) a high-field stage that polarizes the spin system, (ii) a shuttling into zero-field where the original high-field eigenstates $|\uparrow\uparrow\rangle, |\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\downarrow\rangle$, adiabatically transition into the triplet and singlet spin manifolds, and (iii) a final return to high-field conditions in order to probe the fate of the singlet and triplet populations. The group saw both expected and unexpected features upon performing the same experiment under a variety of conditions. Among the expected results was the generation of a long-lived state, which exceeded the polarized lifetimes of each constituent by about a factor of 3; this is the landmark characteristic of a spin singlet eigenstate. Among the experiment's most unusual features was the possibility of creating spin coherence between the triplet and singlet manifolds, whose decay is slower than the actual lifetimes of each one of the states that it involves. In spectroscopic jargon one could describe this as the creation of a subspace where the effective spin's T_2 is longer than its T_1.

From a practical perspective, this new singlet-spin entity could find applications in hyperpolarized NMR and MRI and in the development of more sensitive NMR probes. The latter could be used to investigate slow biomolecular dynamics or the diffusive behavior of molecules in tissues. But at a more fundamental level, it is likely that the most remarkable impact will be the inspiration that this initial NMR observation may provide for the wider world of quantum coherent control in coupled two-level systems.

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Frydman earned a Ph.D. in physical chemistry (1990) from the University of Buenos Aires. In 1992, after a postdoc at the University of California, Berkeley, he became professor in the Department of Chemistry of the University of Illinois in Chicago. In 2001, he moved to Israel to become professor at the Weizmann Institute, where he currently works in the Department of Chemical Physics. In 2012, Frydman became the director of the Helen L. and Martin S. Kimmel Institute for Magnetic Resonance, and chief scientist in chemistry and biology at the U.S. National High Magnetic Field Lab. Frydman's research focuses on magnetic resonance spectroscopy and imaging in solids, liquids, and under *in vivo* conditions.

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