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2495 Main Street
Buffalo, NY 14214
716-885-4701
fax 716-836-1077

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Putting the 'R' Into the Earth's Field NMR

"Confession is good for the soul", so we're now confessing that our Earth's Field NMR apparatus has been misnamed all along. After all, NMR stands for Nuclear Magnetic **Resonance**, and in our EFNMR apparatus, protons generate an emf while precessing inside a coil residing in the earth's magnetic field -- but they aren't 'in resonance' with anything. In fact, in these free-precession experiments, there's no external signal generator for the protons to resonate with! That's not to say that there are not many wonderful experiments that can be done with this conceptually simple apparatus. There certainly are – just look in the thick manual.

But there are always ***more*** things one can do with a TeachSpin apparatus, and now we've done one of them. We've developed a simple and inexpensive coil system that you can add to your EFNMR set-up, whether or not you have our Field/Gradient Coil system. These new coils are shown in the photo. Ten turns of magnet wire are wound on each of the two square white plastic forms.

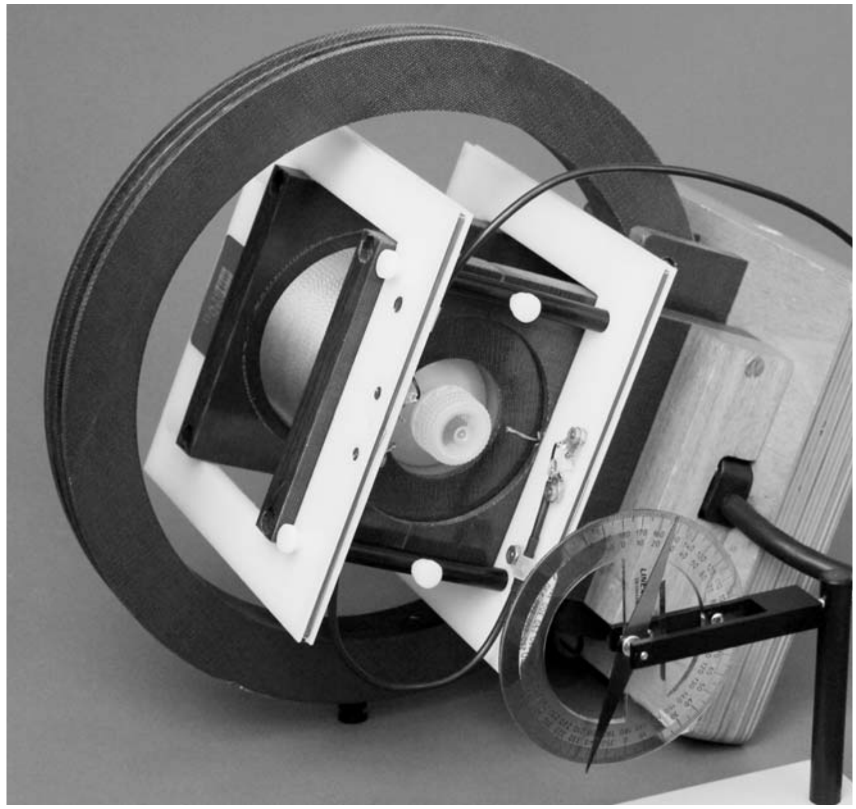

Fig. 1: The new spin-flip coils installed on our Earth's Field NMR 'head'

The purpose of these coils is to create audio-frequency oscillating magnetic fields of very modest strength for brief durations. But those brief, weak fields can have big effects, ***if*** their frequency is ***resonant*** with the precessing protons. The new fields allow your students to observe a lovely phenomenon called a 'spin-echo', widely used in NMR and other branches of physics. Spin-echoes were first observed by Erwin Hahn at radio frequencies, but in this realization the spin-echo gives a signal at a frequency of about 2 kHz, and occurs on a time-scale of about a second, so it can be played right through a speaker and heard in live audio!

How does it all work? To begin the explanation, let's define some directions in space (see Fig. 1). Let the z-axis lie along the local direction of the ambient Earth's magnetic field, B_z, as indicated by the dip needle in the photo; and let the x-axis lie along the axis of the main solenoid. The new square coils give fields along the y-axis that are very nearly uniform over the 125-cm^3 sample volume.

The first step in forming a spin-echo is to create a free-precession signal from the polarized protons in the sample. The protons are polarized by a temporary 50 mT magnetic field along the x-axis established in the main solenoid by a 3 Ampere current for a time comparable to the spin-lattice relaxation time (4-6 seconds for a water sample).

The next step is familiar to users of our EFNMR. That large current is quickly and artfully turned off, leaving the protons polarized along the x-axis, now free to precess in the xy-plane at a rate given by $f_{prec} = (\gamma_p/2\pi)\, B_z$. Those precessing moments act like a spinning magnet, inside a fixed coil, which, by Faraday's Law, creates an emf in the coil. An amplified version of that emf is sent to a speaker, to be heard as a brief 'ping'. An oscilloscope's view of this 'ping' is seen in Figure 2.

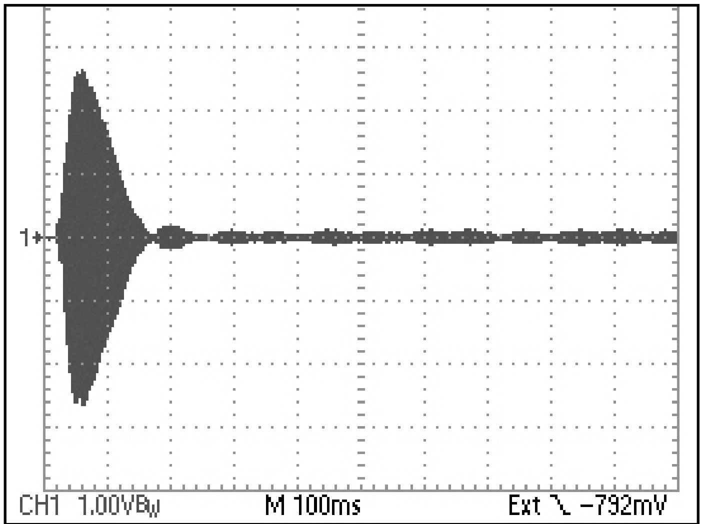

Fig. 2: Envelope of the free-precession "ping"

If the Earth's field magnitude B_z, and the protons' gyromagnetic ratio γ_p, set the frequency of this ping, what sets its duration? In most indoor environments, the duration, of order 0.2 s, is determined by the inhomogeneity, the non-uniformity in space, of the local field strength B_z. It's easy to imagine protons which are initially all lined up along **x**, and which all start precessing together, but which get 'out of phase', as some precess a trifle faster, and some a bit slower, in various places in the sample container. Eventually the proton magnetic moments are pointing in a whole fan of directions, and the sample as a *whole* has no net magnetic moment. So the emf-generation also goes to zero.

This is not the only reason the free-precession signal can go to zero. There is the so called **spin-spin relaxation time** of the particular sample. This relaxation time is the characteristic time of the signal decay, *if the sample were in a perfectly uniform magnetic field.* It is caused by the stochastic fluctuating ***internal*** magnetic fields of the protons themselves and by any other magnetic species in the sample. This time is characteristic of the sample and not of the instrument. It is part of the information that experimenters wish to extract from their measurements. But it can be (and usually is) masked by the nonuniformity of the magnetic field.

Hahn's great invention allows the experimenter to determine directly the spin-spin relaxation time, even with an inhomogeneous magnetic field. He realized the "decay" due to the inhomogeneity could be "recovered" using a resonant time-dependent magnetic field that would flip the spins 180 degrees. This would cause a rephasing of the spins and produce a spin-echo.

The desired intervention is to cause a 'spin flip' of the protons. The necessary rotation about the y-axis can be created by a pulse of oscillating magnetic field in the y-direction, of amplitude B_{osc}, of frequency f_{osc}, and of duration T. But for the desired 180° spin-flip, we need to fulfill two conditions: $f_{osc} \approx f_{prec}$, and $(\gamma_p)(B_{osc}/2)(T) \approx \pi$. In fact, the predicted result for a spin-flip can be derived either from a classical Bloch-vector model, or from a quantum-mechanical treatment of a spin-1/2 two-level system in a magnetic field

$$\mathbf{B} = \hat{\mathbf{z}}\, B_z + \hat{\mathbf{y}}\, B_{osc} \cos(2\pi\, f_{osc}\, t)\ .$$

In practice, we might have $f_{prec} \approx 2$ kHz, and so we would pick f_{osc} to match it. In practice, a pulse of just 20 cycles' duration will suffice ($T = 20 \times 1/f_{osc} \approx 10$ ms). And, for the coils we've built, a current of amplitude just 25 mA (easily produced by a signal generator) is sufficient.

The spin-echo does not appear right after this 10ms pulse; rather, you have to wait for another (say) 0.4 s. That pulse changes the 'fast precessors' which were in the lead at t = 0.40 s into protons which are 'trailing the pack' at t = 0.41 s. Similarly, the 'slow precessors' find themselves leading the pack at t = 0.41 s. So for the next 0.4 s, the protons in higher-B_z regions, still precessing faster, play 'catch-up', until, at around t = 0.8 s, the whole pack has re-assembled into a fully-polarized whole. Fig. 3 shows the 'scope's record of the phenomenon. The coil-to-coil direct pickup marks the time of the 180 degree pulse. The broad peak at the right is the spin-echo envelope. That whole waveform is directly audible, and the 'echo' has the same frequency, and double the duration, of the original ping.

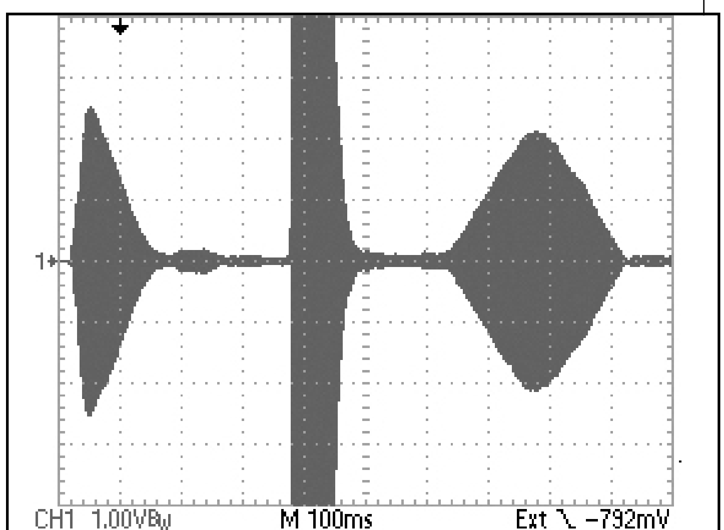

Fig. 3: Free-Induction-Decay ping at left, spin-echo at right

What's the point of this demonstration? The existence of the spin-echo proves that the protons remain "covertly" organized well past the duration of the first free-induction decay. In fact, a careful measurement of the decays of a series of echo envelopes will yield the true spin-spin relaxation time. This, and other pulse sequences, revolutionized the entire field of NMR.

But more broadly speaking, we can view this experiment as telling us, with the strength of each echo, the results of a quantum-mechanical experiment on a collection of two-level systems. In fact, we can resolve the oscillating field along **y** into two fields, rotating (and counter-rotating) in the xy-plane, each of magnitude $B_{rot} = B_{osc}/2$. If we neglect that counter-rotating field, we're left with a problem that can be solved exactly -- no need to use perturbation theory. The prediction is

$$P_{flip} = \frac{(\gamma_p B_{rot})^2}{(\omega_{osc} - \gamma_p B_z)^2 + (\gamma_p B_{rot})^2} \sin^2\left[\frac{T}{2} \sqrt{(\omega_{osc} - \gamma_p B_z)^2 + (\gamma_p B_{rot})^2} \right]$$

This complicated prediction can be tested in detail, since $\omega_{osc} = 2\pi f_{osc}$, T, and $B_{rot} = B_{osc}/2$ are all parameters we know and control. (The strength of the y-fields from the new coils is 94 μT/A, calculable from their geometry.) Let's examine some of those predictions.

We start by picking the oscillating field's frequency to be resonant with the protons, choosing f_{osc} to match f_{prec}. Then the prediction reduces to

$$P_{flip} = \sin^2 [(T/2)(\gamma_p B_{rot})]$$

Clearly this reaches a (first) maximum at the 'π-pulse condition', $\gamma_p B_{rot} T = \pi$, but it predicts a sine-squared form, with further dips and peaks in the strength of a spin-echo, as B_{rot} or T is varied. In Fig. 4 we show spin-echo strength as a function of the computed size of the rotating field present. The sine-squared oscillations do appear, with a period nearly matching that predicted from first principles.

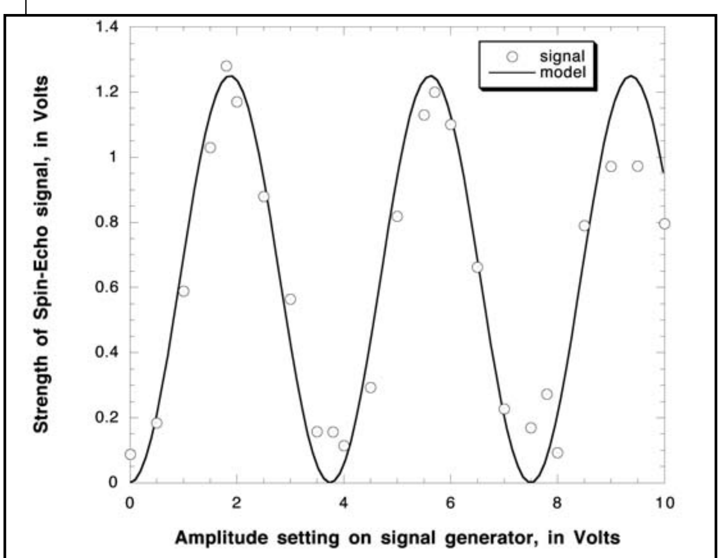

Fig. 4: Spin-echo strength as B_{rot} is varied.

Similarly, in Fig. 5, we see the spin-echo strength measured for a fixed amplitude pulse, with a varying duration T. Again we see the predicted sine-squared oscillations, which are called 'Rabi oscillations' in this context.

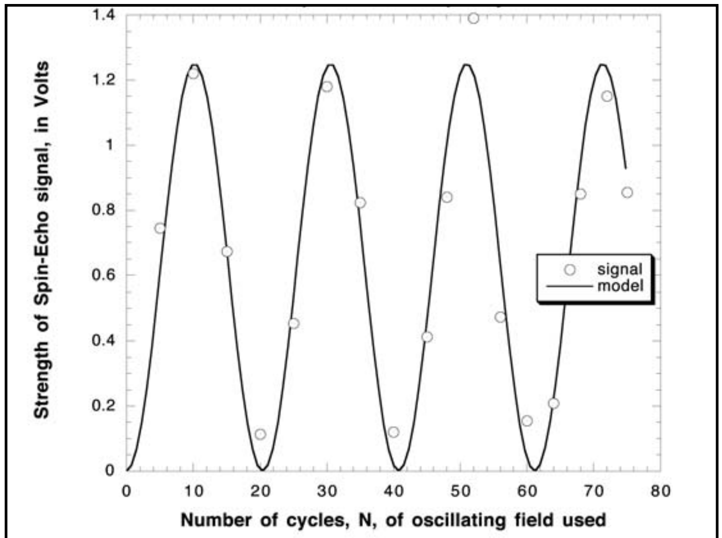

Fig. 5: Spin-echo strength as T is varied.

Finally, in Figure 6, we test for the vaunted resonance, picking a strength and duration for a pulse that matches the optimal π-pulse condition. We vary the frequency of the pulse we inject, and see a lovely resonant peak, with a center and also a width matching the curves predicted by the two-level QM theory. Note that a longer-duration pulse gives a narrower resonant peak. It's legitimate to view the widths of the resonances depicted as arising from the 'energy-time uncertainty principle'.

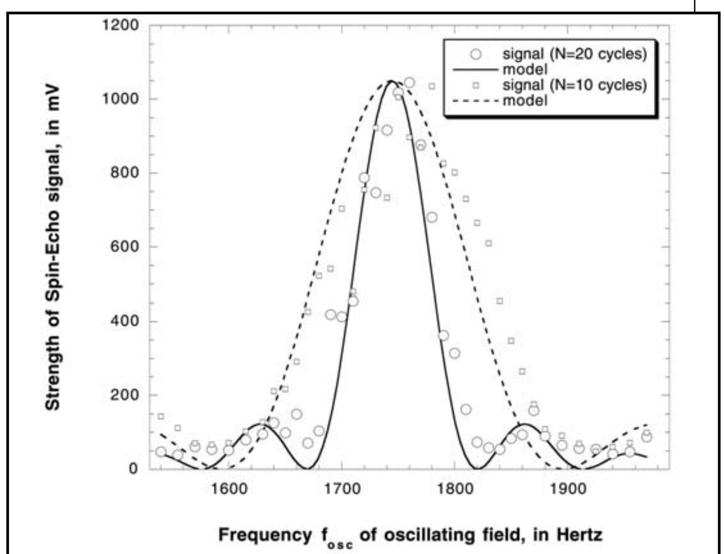

Fig. 6: Spin-echo strength as frequency is varied.

There's a lot of NMR, and plenty of quantum mechanics, in this simple table-top experiment. If you like big-picture thinking, you can view this as a fine example of time evolution, some of which is reversible, and some irreversible, in the thermodynamic sense. And it's all done with audio-frequency waveforms, the addition of time-delay generation and a trigger-able tone-burst generator, using a 125-ml sample of water, in a room-temperature experiment! We hope your students will enjoy it, and learn from it.

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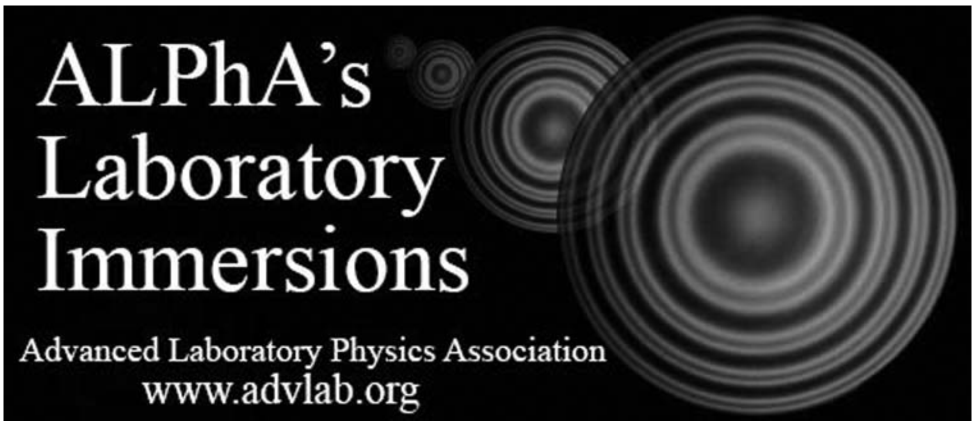

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