The Spin-Flip Coil accessory to TeachSpin's Earth's-Field NMR apparatus

Table of Contents

0. What's a 'spin flip', and why would I want one?

Earth's-field NMR is one of those experiments in physics that depends on spins -- here, the spins of protons, the nuclei of hydrogen atoms in molecules in the liquid state. Everything you can do with EF-NMR depends on what you can do with those spins, using their associated magnetic moments as 'handles'. Thus far, you've polarized the proton spins, and then you've let them precess; but *spin flips* are an example of a new kind of manipulation of spins. Here are some motivations for you:

- Spin flips will allow you to make up for the spatial inhomogeneity that remains in the nearly uniform magnetic field in which your protons precess.
- Spin flips are the tools by which ever more intricate spin manipulations are achieved with nuclei in all sorts of applied NMR techniques.
- Spin flips are illustrations of 'driven quantum transitions', and are thus a model for understanding quantum transitions in many other areas of physics.
- Spin flips are used in NMR imaging (MRI), and even in NMR techniques in quantum computing.
- Spin flips will make available to you the lovely phenomenon of a 'spin echo', and in your EF-NMR case it'll occur at an audible frequency, and on a human time scale.

1. Accessories needed for using TeachSpin's spin-flip coils

a) The TeachSpin EF-NMR (basic) system, including the EF-NMR controller unit and the EF-NMR 'head', plus a dc power supply for the spin polarization.

b) The ability to use these items to produce to produce a proton 'free induction decay' signal, lasting for at least 100 ms.

c) A digital oscilloscope by which to capture such signals.

d) A sine-wave generator of some sort, which can be triggered to produce, on command, a 'burst' of sine waves of chosen frequency, amplitude, and duration. You'll need to be able to cover 1-3 kHz in frequency, 0-5 or 10 V in amplitude, and 1-100 cycles in duration of oscillation.

e) A time-delay generator of some sort, homemade or otherwise, capable of being triggered by a positive rising edge, and of generating (after a chosen delay of 0.5 to 5 s) another edge for triggering your tone-burst generator.

Suggestions for meeting requirements d) and e) are in Section 9.

What you **won't** need to have is

f) The TeachSpin EF-NMR Gradient/Field Coil system and its separate controller unit. If you *do* have this system, and have your NMR 'Sample Head' mounted inside these coils, there is no need to remove it for spin-flip experiments. But you'll be able to do spin-flip experiments with or without this Gradient/Field coil system.

2. **Spin flips, as applied to creating spin echoes.**

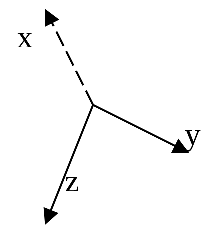
There is some three-dimensional geometry associated with spin flips in the TeachSpin EF-NMR system. It's best understood if you have at hand the TeachSpin EF-NMR 'head' (containing the 125-ml sample bottle), a compass and/or dip needle, and a set of spin-flip coils already mounted on the 'head'.

You'll want to use your compass and dip needle to establish the direction, in 3-dimensional space, along which the local (ambient, earth's) magnetic field lies. Call that direction the ***z***-axis. Next, find a horizontal line perpendicular to that, and call it the ***x***-axis. Then there's a unique ***y***-axis perpendicular to both of these.

Now set up your TeachSpin 'Sample Head' so that the axis of symmetry of the NMR pick-up coil, and of the sample bottle, lie along the ***x***-axis. But tilt the base of your NMR head so that the axis of symmetry of the new, white-framed, spin-flip coils (ie. the axis passing through the center of both square coil forms) lies along the ***y***-axis.

Sample Head with Spin-Flip Coils Mounted

The photograph shows the Sample Head with the white-framed spin-flip coils mounted around the solenoid. The sample bottle is inside the solenoid and the dip needle shows the direction of the local Earth's magnetic field.



The *z*-axis is along the Earth's magnetic field and is parallel to both the plane of the white coil forms and the wooden base of the 'Head'. The *x*-axis goes through the center of the sample and the *y*-axis points into the tilted base.

Why all this fuss? It's to get all your magnetic fields pointing in the necessary directions. Recall that your NMR pick-up coil plays its first role in conducting a sizeable current (1-3 A) for some time (1-6 s), in polarizing your sample. The process leaves the sample with a magnetic moment μ, lying along the ***x***-axis. Once the polarizing current is cut off, that magnetic moment μ precesses around the static earth's field $\boldsymbol{B} = B_z\, \boldsymbol{z}$, so $\mu = \mu(t)$ precesses in the ***xy***-plane, staying perpendicular to ***z***. It's the variation in time of μ_x , the component of μ along the sample-coil axis, which induces the emf in the pick-up coil to generate your NMR signals.

The role of the spin-flip coils is to create *another* magnetic field; this one

- lies along the ***y***-axis, not the ***z***-direction;
- is oscillating in time, rather than static; and
- has a frequency, an amplitude, and a duration which are all under your control.

You'll see that under certain conditions, even a brief (≈10 ms) and weak excitation of these coils can have dramatic effects on your proton spins, with the result of taking each spin and rotating it in 3-d space, by 180° around the ***y***-axis.

And why would you want to do that? For a first experiment, because that intervention can create, apparently out of nothing, the phenomenon of a spin echo. In particular, by this intervention, you can eliminate some of the effects of the spatial non-uniformities in the static magnetic field $\boldsymbol{B} = B_z\,\boldsymbol{z}$.

3. How a 'spin flip' can revive a free-induction-decay signal

This section shows you why proton free-induction-decay signals (FID signals) die away, and what field-inhomogeneity means, quantitatively. It then explains how a spin-flip procedure can counteract these effects.

To make the calculations easier, let's think about an environment in which the static value of the ambient field happens to be exactly 46.98 μT, which is in the right order of magnitude for the earth's magnetic field in some latitudes. That particular value was picked because it translates into a very convenient proton precession frequency.

$$f_{\text{precession}} = (\gamma_p B_z/2\pi) = (42.57 \text{ Hz}/\mu\text{T})(46.98 \text{ }\mu\text{T}) = 2000.0 \text{ Hz}.$$

This means the protons will perform a total of 200.0 turns in space within the first 100 ms of precession.

But inside buildings, or in proximity to iron objects, the ambient magnetic field is not uniform in space, and spatial *gradients* exist in its value. It's routine to find gradients of size (1-5) μT/m in typical indoor environments, and that has consequences even over the volume of an NMR sample bottle. Typical protons in the 125-ml sample bottle in your Earth's-Field NMR experiment are at a distance of order 2 cm away from the center of the bottle, so a typical gradient of 2 μT/m translates into a difference of (2 μT/m)(0.02 m) = 0.04 μT relative to the center of the sample. This gradient means there are protons in the sample experiencing field strength not just of 46.98 μT, but also of (46.98 ± 0.04) μT. Thus protons at various locations experience precession frequencies of not just 2000 Hz, but also (2000. ± 1.7) Hz. In a precession time even as short as 100 ms, various protons precess through not just 200.0, but also (200.0 ± 0.17), turns in space.

While this barely 0.1% variation in the precession frequencies may seem trivial, the spread in amounts of rotation has dramatic consequences. If some protons precess through only 199.75 turns, while others rotate through 200.25 turns, then there will be groups of protons that have gotten fully *half a turn out of phase* with other groups. To put it geometrically, if all the protons were polarized in the ***x***-direction at time $t = 0$, now at time $t = 100$ ms, there is no unique direction in which all the protons are pointing. Instead, the spins are spread out in a 'fan' of directions, all still in the ***xy***-plane, but spread out throughout a wide angle. In our example, it won't be much longer until the proton spins have fanned out to fill a whole circle, at which point the sample's *net magnetic moment* will average to a near-zero value just because of this spread over a range of angles.

So even if individual protons continues to precess for many seconds (and they do!), the sample as a whole loses its magnetic moment in a much shorter time, given the presence of field inhomogeneities. The larger the sample, and the larger the field gradients, the sooner this happens; and once the average magnetic moment is gone, the average emf induced by the precessing protons drops to zero too.

This is the 'dephasing' process that accounts, in typical cases, for the bulk of the decay of the proton free-induction-decay signal. It is, of course, the motivation for the use of the 'gradient coils' in the EF-NMR Gradient/Field Coil part of this apparatus. But with or without such coils, there is always some non-uniformity in the field, and some dephasing of protons, to contend with.

Here's how to understand the role of a spin-flip pulse to counteract the effects of gradient-induced dephasing. We suppose that via some 'magic wand', we can intervene instantaneously, say at time t = 100 ms in the example above, and that our intervention is to rotate each proton's spin direction, by a rotation of 180° in space, about the ***y***-axis. It helps for you to <u>draw a diagram of a collection of vectors</u>, originally all along the +***x***-axis, but now spread out in a fan in the *xy*-plane, having turned through 199.83, or 200.00, or 200.17 turns at time t = 100 ms. If that flip-around-***y*** operation could be conducted instantaneously,

> the protons formerly pointing at the 200.0-turns direction would instead be pointing at the 200.5-turns direction,
> the protons formerly pointing at the 199.83-turns direction would instead be pointing at the 200.67-turns direction, and
> the protons formerly pointing at the 200.17-turns direction would instead be pointing at the 200.34-turns direction.

The point of this 'flip' operation is that protons formerly 'in the lead', 0.17 turns ahead of the pack, will now be 'behind the pack'; and similarly protons that were formerly 'trailing the pack' are now in the lead.

At the end of the 'flip' operation, the precession resumes (in actual fact, it was going on all along, even during a spin-flip operation of finite duration). One important thing has *not* changed: those protons which were in higher-than-average B-field locations will still be in those locations, and will still precess faster than average. And the same will be true for protons in the lower-than-average B-locations. Now, however, the former 'leaders' and 'trailers' have changed places. For a time interval which, in this case, lasts 100 ms, the fast-precessers play a sort of catch-up with the slow precessors which were vaulted into the lead by the spin-flip operation. In this example, at a time just 100 ms after the intervention, all the deficits (or excesses) of rotation have been made up for, and at t = 200 ms, all the protons will have turned through 400.5 turns in total.

At, and in the neighborhood, of that time, all the effects of 'dephasing' will have disappeared, and all the protons will be precessing in unison, and the sample as a whole will then be inducing in the pick-up coil a signal as big as it was at the beginning of the spin precession. Because of the location in time of this re-phasing, the signal that emerges is called a 'spin echo'.

The same 'rephasing' argument still works even if the dephasing due to different rates of precession has gone on much longer. If, in the example above, we had waited not 100 ms, but 500 ms, to intervene, we'd find dephasing by not ±0.17 turns, but ±0.85 turns, and we'd find a proton sample with spins pointing every which way. Right after the proper spin-flip pulse, the spins would *still* be pointing every which way; but their directions would be such that, another 500 ms into the future, the spins would all have rejoined into a single pack, pointing in a single direction.

It's quite remarkable that this spin-flip intervention can seem to 'reverse time' in its dephasing effects. It's an example in real life of the thought-experiment called a 'Loschmidt reversal' in kinetic theory, and in this case it succeeds in reversing the effects of non-uniform field strength. There's a lovely tabletop demonstration of the effects of this sort of time-reversal in fluid mechanics, called an 'unmixing' demonstration, in Am. J. Phys. **28**, 348-353 (1960) and nowadays visible on YouTube videos.

This picture of the effects of a spin flip makes some assumptions, which can now be addressed.

a) In the argument above, it assumes that protons at high-field location before the spin flip *stayed* at high-field locations in space after the spin flip. Any mechanism that causes protons to *move* within the volume of non-uniform field can defeat this assumption, and will lessen the effectiveness of the spin flip. One such mechanism is the diffusion of molecules of the sample in their fluid environment. An easier one to study is mere mechanical motion of the liquids in the sample bottle -- you can imagine the effects of a continual stirring of the sample in defeating the effectiveness of a spin-flip operation.

b) In the argument above, there's the additional assumption that each proton moment stay fixed in magnitude, and that the sample's total moment decays in time due only to dephasing. But in practice, even in a totally uniform (external) field, there is dephasing due to internal interactions. These are called 'spin-spin relaxation' effects, and they effectively cause the spin-precession signals to decay exponentially with a time constant traditionally labelled T_2. So even in an ideal environment, the signals would decay as $\exp(-t/T_2)$. In practice, samples might have a T_2-timescale of whole *seconds*, so a non-uniform magnetic field will cause signals to decay much faster than they would have, intrinsically.

One of the main attractions of spin-echo methods is that they make it possible to see what part of the spin dynamics are due to intrinsic dephasing, by allowing a reversal and elimination of the effects due to extrinsic causes like field non-uniformity.

4. What your spin-flip coils produce, and what effect it has

This section shows you how to understand how you can use the spin-flip coils to create a fully-known magnetic field on the sample. It's all done by keeping track of the current flowing in the coils.

Electrical access to the spin-flip coils is via the little plastic box at the end of their black cable. You'll see a BNC connector labelled DRIVE, and another labelled MONITOR. (There is also a pair of banana plugs allowing direct access to the coil windings, which you won't need to use.) The little schematic diagram on the box shows that if you connect an ac (or dc) generator) to DRIVE, you'll drive a current $i = i(t)$, through the coils. (There are two coils, one on each of the two white plastic coil forms, and they are connected to be electrically in series, and so as to be magnetically additive at the sample's location.) That current $i(t)$ will also pass through a 50-Ω resistor in the box, making available a MONITOR signal $V_{mon}(t) = i(t) \cdot 50\ \Omega$.

Now the coils are arranged in space so as to create a magnetic field which is spatially rather uniform over the sample-bottle's volume, and which lies chiefly along the $\boldsymbol{y}$-direction. If the coils produce a field $\boldsymbol{B}(t) = \boldsymbol{y}\, B_{osc}(t) = \boldsymbol{y}\, k\, i(t)$, where k is a 'coil constant', then an oscillating current

$$i(t) = i_0 \sin \omega t$$

will give a spin-flip field

$$\boldsymbol{B}(t) = \boldsymbol{y}\, B_{osc}(t) = \boldsymbol{y}\, k\, i_0 \sin \omega t.$$

That oscillating-along-$\boldsymbol{y}$ field can be written as the superposition of two fields, each of which is *rotating* in the xy-plane:

$$\boldsymbol{B}(t) = (k\, i_0/2)[\boldsymbol{x} \cos \omega t + \boldsymbol{y} \sin \omega t] + (k\, i_0/2)[-\boldsymbol{x} \cos \omega t + \boldsymbol{y} \sin \omega t].$$

The value of this decomposition is that one of these fields, rotating in the xy-plane at angular frequency ω, and with fixed magnitude $(k\, i_0/2)$, will have a strong effect on precessing spins in the sample. The other of these fields will be rotating in the *opposite* sense in the xy-plane, and will have a negligible effect on the precessing spins. The part of the field that has a big effect is called the 'rotating field', and its effect is largest if its angular speed of rotation nearly matches the precession rate of the spins. The other part of the field is called the 'counter-rotating term', and has a negligible effect under these circumstances -- so we'll neglect it hereafter.

One of the attractions of the TeachSpin spin-flip coils is that you can reliably calculate the size of the magnetic field they produce. Suppose you have a generator with a 50-Ω output impedance, set to give a sine-wave output of amplitude 2 V into an open circuit. Hooked to the DRIVE input of your coils, it'll drive a current through its own internal impedance of 50 Ω, through the coils' resistance of about 3 Ω, and through the monitor resistor of 50 Ω. You'd get an ac current of amplitude about (2 V)/(103 Ω) = 19 mA passing through the coils. There will also be some inductive reactance in the coils, perhaps decreasing the current a bit from this computed value; but *whatever* the current waveform is, the MONITOR output will allow you a measure of it. If you see a sine wave of 800-mV amplitude at the monitor output, you can infer that a current of amplitude

$i = V/R = 800$ mV/50 Ω = 16 mA
is passing through the monitor resistor, and also through the windings of the spin-flip coils.

Here's how to get from there to the spin-flip field you want to compute:

If there's a current $i(t)$ = (16 mA) sin ωt in the coil, and if the coil has a coil constant of k = 95 μT/A, then the amplitude of the oscillating field created by the spin-flip coils is

$$B_{osc} = (95\ \mu\text{T/A})\ (0.016\ \text{A}) = 1.52\ \mu\text{T}\ .$$

What's relevant to NMR spin flips is that you have created a rotating field, of magnitude *half* this, B_{rot} = 0.76 μT, rotating in the *xy*-plane. (The counter-rotating field, also of 0.76 μT magnitude, has negligible effect.)

A necessary (though not sufficient) condition for creating the desired 180° (or π-radian) spin flip is that this field exist for a time T, given by

$$\gamma_p\ B_{rot}\ T = \pi\ ,$$

where γ_p = 267.5 (rad s^{-1})/ μT is the gyromagnetic ratio for protons. Using $\gamma_p = 2\pi\ c_p$ with c_p = 42.57 Hz/μT, this gives the requirement as

$$c_p\ B_{rot}\ T = 1/2,$$

and for the numbers above, requires

$$(42.57\ \text{Hz}/\mu\text{T})\ (0.76\ \mu\text{T})\ T = 1/2\ ,$$

or $T = 0.5/(0.76 \cdot 42.57\ \text{Hz}) = 15.4$ ms.

The point is that there's a firm line of evidence which connects all the way from the observable MONITOR signal the coils' connector box, to a quantitative prediction of what effect the spin-flip coils ought to have on the nuclei in a hydrogen-containing sample.

5. Executing the simplest spin-flip experiments

This experiment will provide you with an audible spin echo from a proton sample.

For starters, you'll need to be able to get a free induction decay (FID) signal from a proton sample (independent of any use of the spin-flip coils). For that, you might want a 125-ml sample bottle filled with tap water, mounted inside the pickup coil in the NMR head. You might want to use ≈3 A of polarizing current (provided by an external dc power supply), for ≈4 s of polarizing time, to polarize your proton sample. You'll want the tuning-capacitor switches on your EF-NMR controller set so that the LC-resonant frequency of the coil-capacitor combination matches the precession frequency of protons in your ambient value of static magnetic field. You'll want to connect the pre-amplifier output of your EF-NMR controller to a 'scope, set to perhaps 50 mV/div vertically, and perhaps 50 ms/div horizontally. And you'll want to trigger that 'scope using the TRIGGER OUTPUT of the EF-NMR controller; set the 'scope to trigger on a positive slope and a positive level of about 1 V.

Then a single push of the START button will give you about 4 seconds of polarization time, followed by a trigger event which you may label as $t = 0$. Starting at $t = 0$, your 'scope ought to show some signal emerging from the pre-amplifier. Part of this signal, from $t = 0$ until $t \approx 50$ ms, is the 'coil transient' -- it'll be there whether you have a sample installed or not. But another part of this signal, the part dominant from $t \approx 50$ ms onwards, should be due only to the presence of the sample.

This signal-from-sample is the FID signal attributable to the protons in the sample. You can try to peak up its strength by fine-tuning the capacitor setting in your LC circuit. The duration of this FID signal is <u>un</u>predictable, since it's controlled by the size of the magnetic-field non-uniformities over your sample bottle's volume. If there is even 100 ms of decent FID signal, you'll now be able to get a spin echo.

Before going on to do so, it's important to find a way to measure the *frequency* of oscillations in your FID signal to modest precision (≈10 Hz). The result will of course depend on the strength of the ambient field, B_z, at your location.

[If you have the Field/Gradient part of the TeachSpin EF-NMR system, you can use the gradient-coil adjustments to improve the homogeneity of your static field, and thus improve the duration of your FID signal. But for spin-echo measurements, you *don't* actually want an optimally long-lasting FID signal, but instead an FID signal that basically died away to the baseline noise level by $t \approx 0.5$ s or sooner.]

Now you're finally ready to use the spin-flip coils to create a spin flip, and thereby a spin echo. What you want to do is to create a 'burst' of sine-wave excitation in your spin-flip coil, at a time like $t \approx 0.5$ s (when the FID has died away). If everything is adjusted optimally, you'll see the FID *revive*, reappearing *not* at $t = 0.5$ s, but *later* in time, in fact centered around the point $t \approx 1.0$ s. If everything is right, the effect is <u>not</u> small -- the revived signal will be nearly as large in size, and of *double* the duration, as your original FID signal. That's the spin echo.

So you'll need a way to derive, from the pulse that's triggering your 'scope at $t = 0$, another pulse occurring at (say) $t = 0.5$ s. This later pulse needs to be of a size and duration suitable for triggering your sine-burst generator. [The Appendix suggests some ways to do this.]

The generator needs to be set correctly, too. The chief requirement is for its frequency nearly to match the protons' ongoing precession frequency, to a modest precision of perhaps $\pm 1\%$, The second requirement is jointly on its amplitude and its duration; try starting with a generator set to deliver a burst of about 2 V amplitude, and a burst of 20 cycles' duration of sine wave.

If you see evidence of a spin echo on the 'scope, you'll be able to *hear* it too. Use the right setting of the TUNING of the main-amplifier section of the EF-NMR controller to optimize its gain the at the frequency of your FID signal, and it'll thus be able to send onward both the original FID, and the revived spin-echo signal, from the pre-amplifier, through the (tuned) main amplifier, to the speaker. Now you should hear, after the polarization interval, the sequence in time of the FID signal, a click at the occurrence of the sine-wave burst, and then, later still, the spin echo itself.

Notice that the brief ($\approx$10 ms duration) tone-burst signal sent into the spin-flip coils will also couple (capacitively) to the NMR pick-up coils around the sample, so that you'll be able to see, right on your 'scope record, an indication of when in time the tone-burst occurs. The spin-echo signal will come at a predictable *delay* after this marker of the tone burst. If you can vary, from shot to shot, the time delay (0.5 s in the discussion above) at which you apply the tone burst, you'll be able to see the effect that has on the location in time of the spin echo. And you'll see why the poetic term 'spin echo' was invented for this process.

Once you've seen a spin-echo signal, adjust the amplitude of your tone-burst generator, up or down, to optimize the strength of the spin echo signal. You'll know you have a genuine spin-echo phenomenon if, upon *doubling* the generator amplitude compared to this optimal setting, you get just about no spin echo at all! The reason is that a double-strength intervention will give you a '2π pulse' in place of the desired 'π pulse', and the result is a no net spin flip, and so no revival of the signal.

There are other experimental tests that a genuine spin-echo signal has to fulfill, some of them of amazing subtlety. The model above clearly claims that the precessing spins in the sample bottle are literally the spinning generator which creates the spin-echo signal by Faraday's Law of Induction. If follows that if the sample bottle is removed from the sample space, after the initial FID (whether before or after the spin-flip intervention), then there can be no spin-echo signal. (Try it!) Less obviously, if the water in the sample bottle is moving, due to the bottle having recently been vigorous swirled, then the spin-echo effect will be decreased, since you can no longer count on protons being in the same location in space for their dephasing and rephasing intervals of time.

To investigate this latter effect more systematically, it's fun to build a sample bottle in which protons are locally in a liquid environment, but in which they are mechanically nearly tied to the bottle. One way to do so is to stuff an empty sample bottle with glass wool, and then to fill it with water; the glass wool partly 'immobilizes' the water. Even more effective is to fill a sample bottle with (liquid-state) gelatin (ordinary, even flavored, Jello™ works fine) and then let it set to a 'solid'. Either way, you can confirm that you can get an ordinary FID, and then a normal spin-echo effect, from your new samples. The truly subtle experiment now consists in causing a one-time rotational displacement of the sample bottle, by perhaps a quarter-turn, about its own symmetry axis (the x-axis) during the spin experiment. (You're moving, but not *re*moving, the sample bottle during the experiment.) The prediction of the modeling above is that such a rotation, conducted either just before or just after the spin flip, will defeat the rephasing mechanism (why?), and thus abolish or diminish the spin-echo signal. Quite apart from forming a detailed confirmation of all the theoretical modeling above, the relevance of this demonstration to flow studies in hydrodynamics ought to be obvious.

6. What you can investigate systematically on spin flips

If you're set up to create,

at a fixed time delay T_{delay} after $t = 0$,

a tone-burst into the spin-flip coils,

and if you're seeing,

in the vicinity of $t = 2\ T_{delay}$,

a spin-echo signal from your pre-amplifier or amplifier output,

then you're ready to investigate the detailed predictions of theory for the effectiveness of the spin-flip intervention.

The claim is that the probability of a spin flip, and therefore the relative strength of the spin-echo signal, is given by

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

where B_z is the strength of the static field in the $\boldsymbol{z}$-direction, B_{rot} is the magnitude of the rotating field, which rotates at angular frequency ω_{osc} in the xy-plane, where γ_p is the nuclear gyromagnetic ratio, and where T is the duration of the intervention. This can be more usefully translated into the language of ordinary (rather than angular) frequencies by defining $f_{prec} = (\gamma_p\ B_z)/2\pi$ as the precession frequency of the protons, and f_{osc} as the frequency of the oscillating current sent by the generator into the spin-flip coils. It's also useful to introduce $c_p = \gamma_p/(2\pi)$ as a version of the gyromagnetic ratio, but in units of Hz/T [rather than (rad/s)/T]. We find

$$P_{flip} = \frac{(c_p B_{rot})^2}{\left(f_{osc}-f_{prec}\right)^2+(c_p B_{rot})^2}\sin^2[\pi T\sqrt{\left(f_{osc}-f_{prec}\right)^2+(c_p B_{rot})^2}] \quad .$$

This allows an investigation of the separate roles of the

frequency f_{osc}

duration T

and strength B_{rot}

of your tone-burst intervention.

It is probably best to start with the tone-burst generator's frequency f_{osc} set to lie at your best estimate of the proton precession frequency, and to make B_{osc} or T your first independent variable.

If you fixed T, the duration of the tone burst, to be 20 cycles' duration, you'll find that you can vary your generator's amplitude over a wide range, perhaps 0-10 V, and find a complicated variation of size of spin echo. Concentrate first on the 0-2 V range (in which the spin-echo signal strength should rise toward a maximum), then in the 2-4 V range (where the signal should peak and then drop again). The reason for this behavior is that the $f_{osc} = f_{prec}$ limiting case of the formula above is

$$P_{flip}\left(f_{osc} = f_{prec}\right) = \sin^2\left[\pi c_p B_{rot} T\right] \quad ,$$

which reaches a maximum (of 1) at the 'π-pulse' setting

$c_p\ B_{rot}\ T = 1/2$,

but which falls again to a minimum (of 0) at

$c_p B_{rot} T = 1$.

(Remember that each new observation of spin-echo strength is a wholly new experiment, starting with a few seconds' polarization time, a brief occurrence of the FID signal, a wait until you intervene with a spin-flip pulse, and another wait until the spin-echo signal reaches a maximum. So you'll get a new data point on your curves only every 10 s or so.)

Once you've explored this (or a larger) range, set the generator's amplitude to that value which gave a peak (ie. a π-pulse), and now explore the effects of varying duration T, say from 10, through 20, to 40 cycles' duration. Again you should see evidence of sine-squared oscillations in spin-echo strength.

Once you have a combination of B_{rot} and T which you're sure is giving you a π-pulse, fix these two values, and try the effects of varying f_{osc} (the frequency of your tone burst). Try varying f_{osc} over a range of $\pm1\%$, then $\pm2\%$, then $\pm5\%$, relative to your previous center. In practice, it might be easier to keep constant the *number of cycles* of oscillation, N, in the spin-flip pulse. If you have a combination of field strength B_{rot} and duration T, namely N cycles of oscillation at f_{osc}, which gives an optimal π-pulse at $f_{osc} = f_{prec}$, and then you keep N constant while you vary f_{osc}, the prediction for spin-flip probability becomes

$$P_{flip} = \frac{1}{1+(\frac{2N}{f})^2(f_{osc}-f_{prec})^2} \sin^2[\frac{\pi}{2}\sqrt{1+(\frac{2N}{f})^2(f_{osc}-f_{prec})^2}] \quad ,$$

which again displays a maximum (of value 1) at $f_{osc} = f_{prec}$.

Collecting enough data points, you should see the 'resonant peak' predicted by the appropriate limit of P_{flip}, reaching a maximum when $f_{osc} = f_{prec}$, and dropping down to zero at locations to either side of f_{prec}. The width-in-frequency of this peak is fixed chiefly by your choice of T, the duration of the intervention you're using; if you stick with N=20 cycles' duration, the full width at half maximum of your 'resonant peak' will be about 4.0% of the precession frequency. The *larger* you choice of T (or number of cycles N), the *narrower* this peak will be. This may fairly be called an illustration of the 'energy-time uncertainty principle'.

The location in frequency of this peak is thus a measure of f_{prec}, the precession frequency of the protons in your ambient field. What you've done is to find what frequency of rotation-in-space of the rotating component of the 'intervention field' best matches the frequency of the precession-in-space of the proton spins themselves -- that's the condition for the most effective spin flip.

There's another viewpoint on this result, even more directly tied to quantum mechanics. You may view the static magnetic field B_z as creating a splitting in energy between the spin-up, and the spin-down, orientations of the nuclear spin. It's easy to show that the energy difference between these (now non-degenerate) energy eigenstates is

$$\Delta E = \gamma_p B_z \hbar \quad .$$

Now you may view your added, time-dependent, oscillating field in the ***y***-direction as *driving quantum transitions* between these two states, and driving them resonantly when the energy of its photons, given by

$$E_{photon} = \hbar\omega_{osc} \quad ,$$

matches the energy difference between the two spin states. This use of the ordinary 'Bohr condition' reproduces the prediction that spin flips will be most effective when $\omega_{osc} = \gamma_p B_z$, or when $f_{osc} = c_p B_z = f_{prec}$.

[However interesting your result, this is probably not the most *efficient* way to measure f_{prec}; you can get a better estimate of its value, in a lot less time, by taking a record of a single occurrence of the FID signal, and forming its Fourier transform. The peak of that Fourier transform will tell you f_{prec} for a 'single shot' observation. The effectiveness of this procedure is the basis for Fourier methods so widely used in NMR nowadays.]

Back to your data: notice that your frequency scan over f_{osc} reveals the zeroes of either side of f_{prec} predicted by the equations above. By artful choice of T, you can make these 'nulls' fall where you wish in frequency space. By this means, you could arrange to spin-flip all the protons in your sample (precessing perhaps at 1900 Hz), but to leave *un*-flipped all the fluorine nuclei in your sample (precessing as they would at ≈ 1790 Hz). This is one example of the many artful, and *selective*, spin manipulations that are used by NMR practitioners.

Note finally that out beyond these zeroes, the spin-flip probability is predicted to have some subsidiary maxima. You can compute where these should occur, then confirm that they exist, and (hardest of all) try to come to some sort of mental picture of why they occur.

7. What you can investigate systematically *with* spin flips

This section assumes that you've seen a spin echo (section 5), and that you've assured yourself that you're optimally generating an on-resonance π-pulse (section 6). What does that make possible?

The first thing you can check is the strength of the spin-echo signal, as measured perhaps by the rms size of the oscillations it shows in the vicinity of its center. Here's a way to persuade yourself that the spin-flip mechanism really works to revive the original FID signal -- the method depends on comparing

> a) the biggest signal you can get (given the presence of field gradients) at the center of the spin echo, versus
>
> b) the biggest signal you can get, at that same time after $t = 0$, with*out* using any spin-flip pulse, by trying instead to cancel out all the effects of gradients.

This comparison depends on the availability and use of the EF-NMR Gradient/Field Coils. The point of the comparison is this: method b) gives a long-lasting FID signal, which might have as an envelope an exponential decay curve. We'd write it as $\exp(-t/T_2^*)$, where the decay time T_2^* is attributable both to intrinsic relaxation of the size of spin magnetic moments, and to residual dephasing effects due to leftover field inhomogeneity. But typically the decay time T_2^* is still shorter than the true, ie. the intrinsic, spin-spin dephasing time T_2.

To prove that is the task of method a). The goal is to show that a) can give, for the fixed location in time at the center of the spin echo, a larger signal than b) can deliver (at this same point in time). The claim is that, under conditions of a perfect π-pulse for the whole of the sample, the strength of the revived FID signal will be governed by $\exp(-t/T_2)$, where t is the time-location of the center of the spin echo. That is to say, method a) ought to reveal the effects of spin-spin relaxation only, *un*complicated by the additional effects of field inhomogeneity.

So, concretely, if you intervene with a π-pulse at time $t = 0.5$ s after the start of an FID, you'll get a spin -echo signal peaking around $t = 1.0$ s. And the claim is that at the peak of the echo you'll be getting a *bigger* signal than you can get in the vicinity of $t = 1.0$ s, even by your best efforts at method b).

Here's another application of spin echoes, one *not* requiring the use of gradient coils. The payoff is getting the 'echo of an echo', and the effect is the most enjoyable if you can trigger a π-pulse at will, via fingertip push-button command.

The procedure might be to get a usual FID signal, decaying rapidly, and to intervene with a π-pulse at around $t = 1$ s. You expect, and should hear, a spin echo around $t = 2$ s. Now what happens if you create *another* π-pulse intervention, this one at $t = 2.6$ s? It's been 0.6 s since the spins were optimally re-phased; they should therefore re-phase again, and give another echo, this one centered at $t = 3.2$ s.

The pleasure of this method is that it's entirely up to you to decide, *in real time*, when to intervene with a first, and then with a second, π-pulse. A single oscilloscope record can be arranged to show the original FID, both interventions, and both echoes, all laid out in time.

Once you've seen the 'echo of an echo', and understood how it arises, you're ready to create a series of multiple echoes by using a series of π-pulses. You stand ready to harvest a T_2-value from a single (long) record of the relative strength of multiple echoes. To make this sort of investigation repeatable, you'll want to devise some sort of 'pulse timer', to initiate π-pulse interventions at a chosen and repeatable set of times, all fixed relative to the original $t = 0$ start pulse.

Suppose you get an FID signal of brief duration starting at $t = 0$, and that it's decayed basically to baseline noise at $t = 0.3$ s. Then clearly your timer can intervene with a π-pulse at $t = 0.3$ s, and you'll get a first spin echo signal centered around $t = 0.6$ s. Then a second intervention at $t = 0.9$ s will give a second spin echo centered at $t = 1.2$ s. A third intervention may come at $t = 1.5$ s, giving a third echo centered at $t = 1.8$ s, and so on. (Note the requirement of a series of delays of T, $2T$, $2T$, $2T$ ...) The peak sizes of each spin echo will give you a series of samples, taken at $t = 0.6$, 1.2, 1.8 s and so on, of what should be the function $\exp(-t/T_2)$. So the appropriate graph of echo strengths -- all obtained in one long 'scope recording of the signals following a single START -- plotted as a function of time, can give you the (true) T_2 value for your sample.

The method does assume that each π-pulse is giving a perfect 180° spin flip for the whole of your sample; so in practice, this method requires that you've optimized your π-pulse parameters quite carefully. For a check on that, you can try doubling N, the number of cycles of sinusoid in each intervention pulse -- that is to say, you can test the effects of a series of what you think are all <u>2</u>π-pulses. Only if you've gotten a negligible echo after each of these interventions can you be sure that you're delivering a series of accurate 2π-pulses, and in fact you will have proven

a) each is a pulse of the right size, and uniform enough over your whole sample volume, and

b) that there aren't any cumulative errors, even in a series of many 2π-pulses.

Once you've demonstrated such a 'null result' with a series of 2π-pulses, you can be well assured that a succession of pulses, each of half as many cycles of oscillation, will faithfully represent a series of π-pulses. When you've used echoes from a series of π-pulses to extract a T_2-value, you'll have re-created the Carr-Purcell pulse sequence first used in high-field NMR. You'll also have developed a technique capable of precise measurement of T_2 for a given sample, and could then go on to ask the physics question: what *determines* T_2, and how can I change it?

[In these experiments, note that there is no 'r.f.' pulse used at $t = 0$ to initiate the original FID signal, and further, that there is no continually-operating oscillator running at frequency f_{osc}, gated into play successively at each intervention. Hence there is no way to achieve the clever Meiboom-Gill pulse sequence also used in high-field NMR. But in this apparatus, you can create π-pulses so nearly perfect as to render the M-G pulse sequence unnecessary.]

8. The properties of the spin-flip coils

The design of the TeachSpin spin-flip coils is to create a 'square Helmholtz' geometry, using two square coils, each of 10 turns, designed to have, as dimensions, a side S = 172.2 mm, and a plane-to-plane separation of H = 93.8 mm.

The coils are electrically in series, and are connected so that their fields reinforce (rather than cancel) at the center of the coil system. The separation H is chosen to give optimal homogeneity of the field created in the vicinity of the center. The size S is chosen to be about as big as possible, and still let the coil system be mounted inside the bucking coil of the NMR 'head'.

What follows is some discussion of the 'coil constant' k, which gives the field strength By due to these coils, per unit current in (each of the turns of) their windings. The short form of the answer is that $k \approx 95$ μT/A. Because the coils are wound on non-conductive forms, and used in an iron-free and conductor-free environment, this value ought also to apply for alternating currents in the coils.

Here are some methods for computing that k-value:

Start with a single square in the xz-plane, centered around the y-axis and lying at $y = 0$. Let the square extend from $-s/2$ to $+s/2$ in x and z, and let there be a test point at $(0, h, 0)$ on the y-axis. Then each side of the square contributes equally to the field B_y at the test point, and the Biot-Savart Law makes it easy to compute the field component B_y at the test point. One single element of wire, at location $(x, 0, 0)$ on one side of one square, carrying current i, gives

$$dB_y = \frac{\mu_0 i}{4\pi} \frac{s/2}{[x^2+h^2+(s/2)^2]^{3/2}} \quad ,$$

and to take into account the whole of one side, this needs to be integrated over the interval $-s/2 < x < +s/2$. For the whole of a single square 1-turn coil, this method gives

$$B_y = 8 \frac{\mu_0 i}{4\pi} (\frac{s}{2})^2 \frac{1}{h^2+(s/2)^2} \frac{1}{\sqrt{h^2+s^2/2}} \quad .$$

That gives a resource sufficient to solve the problem of interest, in which two such square coils, of side length S, are located in the $y = -H/2$ and $y = +H/2$ planes, and the test point is at $(0, y, 0)$, ie. is at a distance $| H/2 - y |$ from one coil plane, and $| y + H/2 |$ from the other. The result is a complicated function for $B_y(0, y, 0)$, but it is an even function of y. The 'Helmholtz condition' for uniformity is achieved by picking H such that $B_y(y)$ has a vanishing second derivative at $y = 0$. This optimal-flatness condition is achieved for $H = 0.5445\ S$, and that spacing has been built into the TeachSpin coils.

With that choice for H, the field at the geometrical center of the coil combination is given, for a 10-turn winding of each of the two coils, by

$$B_y(center) = 10 \frac{\mu_0 i}{S} (1.2961) \quad ,$$

and for S = 0.1722 m, that gives $k = (B_y/i)$ = 94.6 μT/A. The uncertainty in this value is of order 1%.

One of the attractions of the Biot-Savart method used above is that it can be repeated for an arbitrary test point (x, y, z) near the origin, in an arena in which the two square coils are located in the $y = -H/2$ and $y = +H/2$ planes. The calculation for square-form coils is rendered easier than the traditional circular forms by the fact that the current elements in the coil are everywhere only in either the x- or the z-directions. So any Cartesian component of the Biot-Savart expression ($i\, \boldsymbol{dl} \times \boldsymbol{r}$) can be written down analytically. For a generic test point, the integrations over the eight sides of the two squares need to be conducted numerically, but the result is that B_y (or, if desired, another component of $\boldsymbol{B}$) can be computed for any location of test point.

The results can be used to confirm the k-value derived above, and also to check the homogeneity of the spin-flip field for points not so close to the origin. This will give a way to see how nearly uniform the k-value is for generic points within the sample volume. It will also give a way to see why spin-flip pulses meeting the '11-π' condition would likely be less effective than 'π-pulses': it's hard to achieve so uniform a B_y-field that the '11-π' condition is adequately met for all the spins in the sample.

There's a separate, and NMR-based, method for checking directly the coil constant, the k-value, computed above. It depends on the availability of the gradient coils in the EF-NMR G/FC unit, and their having been adjusted for optimal field homogeneity. This will give proton FID signals of some seconds' duration. The method also depends on a way (perhaps using FFT methods on those FID signals) for extracting the proton precession frequency with high precision. But given those tools, the idea of the method is simple: putting a *dc* current of i into the spin flip coils will generate a field $B_y = k\, i$, and this will change the total field from B_z to $[B_z^2 + (k\, i)^2]^{1/2}$. This motivates a plot, as a function of the chosen current i, of the *squares* of the observed f_{prec} values, to permit the extraction of k.

In practice, it might be enough to vary i over the range -50 mA to + 50 mA, giving a B_y-contribution of about 5 μT. This adds, in quadrature, to a typical B_z-field of 50 μT, to give a total field whose magnitude can be raised by about 0.25 μT. That's only about 0.5% of the typical B_z-value, but this NMR-based method is easily able to detect with some precision these small changes in the precession frequency.

[There are further complications, however; the gradient-cancellation procedure on which this method depends is ideal for correcting the gradients in a field along the +$\boldsymbol{z}$-direction. But the addition of the B_y-contribution of up to one-tenth of the main B_z-field also achieves the rotation of direction in space of the total $\boldsymbol{B}$-field by up to 0.1 radians. And the gradient cancellation will now be imperfect for a field that's been rotated. So there's merit, in this method, of working outdoors (where gradients are smallest), or with a sample container of reduced size (to lessen the effects of gradients over the sample volume).]

Back to coil design parameters: the two coils are each wound with ten turns of #28 AWG copper wire. With one side of one turn of one square having a length S, the complete coil contains length (4)(10)(2)$S \approx 13.8$ m of wire. The resistance of the windings, at room temperature, is thus about computed to be about 2.9 Ω. There is additional resistance in the connections and the cabling, but it is clear that in regular operation, the current in the coils is limited almost wholly by the resistance of the monitor resistor, and the internal impedance of the generator driving the coils.

For excitation of the coils by an ac source, there is an additional consideration of the inductance of the coils. It's easy to do a very approximate calculation of the inductance L, if we approximate that the coils create a field of $B = k\,i$ everywhere throughout a volume of size $S \times S \times H$ (and if we ignore entirely the fringing fields outside the coils' volume). Then we find the volume-integrated magnetic energy of the system is

$$U_{mag} = \int \frac{B^2}{2\mu_0}\, dV \approx \frac{(ki)^2}{2\mu_0} S^2 H \quad .$$

If we equate this to the magnetic energy of an inductor, (1/2) $L\,i^2$, we get $L \approx (k^2/\mu_0)\, S^2\, H$, and evaluating, we find this to be about 20 μH. Clearly, an actual value for the coils could be measured empirically, *in situ*. The relevance of this approximate inductance is to use it to compute the spin-flip coils' inductive reactance at a typical operating frequency of $f = 2$ kHz; the result is $Z_L \approx 0.25$ Ω, smaller even than the dc resistance.

Independent of coil resistance and impedance, in any case, all the current passing through them also passes through the 50-Ω monitor resistor. So the potential difference at the MONITOR output of the coils' connector box is always a faithful surrogate for the actual (time-dependent) current waveform in the coils.

9. Appendix: methods for creating the delay, and the tone burst

The 'tone burst'

Perhaps the simplest way to generate a tone burst on command is to use one of the rather low-priced 'direct digital synthesis' signal generators now available. For example, a Protek B8003FD will generate several kinds of waveforms, including sinusoids, at user-chosen frequencies and amplitudes, and easily covers the range of frequencies and amplitudes needed for earth's-field NMR. It also has a 'burst mode', allowing the generation, on command, of a fixed number of cycles of a sinusoid. The command can be exercised using a front-panel hand-pushed 'trigger' button, or by the arrival of a brief positive-going pulse at a back-panel BNC input.

Of course there are alternative methods. Users enjoying a computer-interfaced environment can easily create a 'virtual oscillator' to create the necessary sine waves via a look-up table and a digital-to-analog computer. Since the waveforms needed in these experiments are sinewaves at audio frequencies, and since a computer might contain a sound card suitable for generating audio frequencies, the necessary hardware might already be present. Since the frequency-precision requirements of the spin-flip experiments are very modest, it won't matter that there is no direct control over the computer's actual time base.

Nor is the use of sinewaves crucial. Even a square-wave waveform at a given frequency contain plenty of the fundamental waveform (which is sinusoidal, and which will drive a spin flip); of course it contains some harmonics too (but they are far off resonance, and will affect a spin flip negligibly). The use of a square wave will make it harder to understand the absolute strength of the rotating spin-flip magnetic fields, however.

Nor does the square wave even need to be symmetrical about zero! A suitably scaled TTL waveform will alternate between voltages near 0 and V, and it is thus the superposition of a dc offset of $V/2$ plus a symmetrical square wave. The dc offset will create, via the spin-flip coils, a small dc field component in the $\boldsymbol{y}$-direction; this will contribute to the total value of the dc field, but only quadratically since it'll typically be much smaller than the ambient field B_z. Meanwhile the ac component will serve to drive a spin flip.

The time delay

The user's environment will dictate what is the easiest way to arrange the tone burst to be delivered at a desired time. Users with a computer-based solution to the tone burst can of course generate the time delay in software, based on the registration, by the computer, of the same input trigger pulse which triggers the 'scope in the usual data-acquisition scheme.

Those using a separate hardware function-generator for producing the tone burst will probably want a hardware time-delay generator. There are commercial devices expressly designed to create such time delays, but in this case the timing demands are so simple and so modest that there is an easy breadboard solution, involving a single chip.

We've used a 7400-series dual multivibrator chip, the 74HC221A, to address the timing needs in two stages:

a) the positive-going trigger pulse emerging from the EF-NMR controller box will trigger a one-shot multivibrator, resulting in a TTL level of HIGH that lasts as long as an external resistor and capacitor dictate. It's easy to achieve a time delay of 0.5 s, and not quite as easy to make this delay time readily variable.

b) the negative-going edge at the end of this 'wide pulse' can be used to trigger the other one-shot multivibrator in the chip, this one arranged to create a brief (≈25 μs) positive-going pulse. The descending edge of that 'narrow pulse' pulse will trigger the Protek generator to create its tone burst, as described above.

This makes a fine project in 'laboratory electronics', easy to achieve if a powered digital breadboard is on hand. The design and verification of correct operation of the time-delay generator, and confirmation that the tone-burst is emerging at the right time, make for a real-life proficiency exercise in electronics, and a good test of a student's facility is using an oscilloscope artfully.