Composite Pulses in Zero-Field NMR

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Composite pulses (1) have been used in NMR for spin decoupling (2), broadband, narrowband, and bandpass excitation (3), spatial selectivity (4), multiple-quantum excitation (5), and more (6). A new area in which their application will be important is zero-field NMR (7) where pulsed dc fields play the role of the radiofrequency pulses of high-field NMR. Broadband behavior is required, for example, to overcome the inhomogeneity of the dc pulses. Narrowband excitation is important in the selectivity between spins and isotopes, for example, if one wishes to apply a zero-field \( \pi/2 \) pulse to carbon-13 spins without affecting protons or deuterium (a feat easily accomplished in high-field NMR because of the frequency differences). Zero-field selectivity is analogous to high-field \( \omega_1 \) selectivity (3k) as shown in Fig. 1. In this communication we demonstrate composite \( \pi \) pulses produced by applying dc fields in different directions in the laboratory frame. The pulse sequences used compensate for the inhomogeneities of the dc fields, in analogy to the 90°, 180°, 90° pulse of Levitt and Freeman (3a-c), and show narrowband \( B_1 \) selectivity (used for selective irradiation of isotopes) in analogy to spatially selective pulses (8). This is useful in zero-field NMR and NQR with pulsed field cycling (7), in zero-field spin echoes (9), and in two-dimensional spectroscopy (10).

Producing the analog of a phase-shifted pulse sequence in zero field requires a cross coil configuration. In this case, a system was developed that is composed of three orthogonal coils with uniform characteristics, such as inductance (which determines risetime characteristics), homogeneity, and field strength (which can be controlled with the voltages and currents used). High-power current pulsers (11) which provide for rapid reversal of the direction of current flow were designed to provide the complementary 180° phase shifts to the \( x, y, \) and \( z \) coils. Thus, six basic directions and their linear combinations of pulses can be manipulated in the composite pulse sequence.

A sample of \( \text{CH}_2\text{Cl}_2 \) in a nematic liquid crystal, a system which when demagnetized in the field cycle shown in Fig. 2, has an initial state proportional to \( I_x \) (9). A comparison of single pulses of nominal pulse angles of \( n \times 180° \) and composite pulses are shown in Fig. 3. The single \( n \times 180° \) pulses were extracted from an experimental curve of signal intensity vs pulse length. Single pulses are seen to produce a curve which decays with increasing pulse length. The decay is due to spatial inhomogeneity of the dc fields. This was verified by varying both the field strength used (which was \( \sim 40 \) G...
FIG. 1. Nuclear spin excitation in high field and zero field. In high-field NMR experiments, spin species may be selectively irradiated on the basis of Larmor frequency. In zero field, the differences in magnetogyric ratio provide a handle for selective irradiation through the relationship, $\omega_l = \gamma B_1$. Excitation of a single spin type by narrowband irradiation in zero field provides for manipulation of initial states and their subsequent evolution in zero field.

FIG. 2. Field cycle using pulsed dc magnetic fields. Demagnetization of the sample to an intermediate field, $B_n$, results in a zero-field state proportional to $I_z$ immediately after the shut-off of this field. Pulsed dc fields (P) can now be applied in a minimum of three orthogonal directions while varying their length and magnitude. The effect of the coherent manipulation of the magnetization in zero field with dc pulsed fields can be monitored by reapplying the $z$ field and remagnetizing to high field where the magnetization is sampled. Field cycling and dc pulsed field times are not drawn to scale.
Fig. 3. Experimental comparisons of single and composite dc magnetic field pulses. The sample is CH$_2$Cl$_2$ in a nematic liquid crystal which has a proton dipolar coupling of approximately 2 kHz. Pulsed fields used were on the order of 45 G for all directions. In (a), a single pulses of n $\times$ 180°, chosen from a function of signal intensity vs pulse length, are shown to cause the magnetization to decay rapidly with increasing pulse length. In (b), using concatenated composite pulses of 90°, 180°, 90°, the behavior is slightly improved. To reduce the cumulative errors in repeated 180° pulses, a phase cycled pulse 90°, 180°, 90° was alternated with 90°, 180°, 90° in (c) yielding an improvement in the long-term behavior.

and much larger than the averaged dipolar interaction of $\sim$0.5 G) and the sample volume.

Using composite pulses, the n $\times$ 180° and n $\times$ 360° rotations of the magnetization are seen to show some improvement as the result of compensation. In both the single- and composite-pulse cases, cumulative errors in the pulses result from long sequences. When larger pulse angles are needed, the efficiency can be improved to some extent by phase cycling the second pulse of the composite sequence. Figure 3c illustrates this effect by using (90°, 180°, 90°, 90°, 180°, 90°) sequences. The compensation is improved on subsequent pulses and can be understood by the fact that the reverse sense of rotation of the 180° and 180° pulses corrects for some of the error due to the 180° pulse and returns the magnetization more effectively to the +z axis.

Composite pulses which are isotope selective may also be applied in zero field. Any pulse which is narrowband in $\gamma B_1$ in zero field (generally described as spatially selective with respect to $B_1$ when using a surface coil in high field) will act as an isotope selective pulse on the basis of the magnetogyric ratio. These pulses may be used to alter the initial condition of a heteronuclear spin system in zero field prior to evolution and
thus discriminate against specific spectral frequencies. Similar experiments using rf pulses to effect the same results have been reported previously (12). Experimental results using the zero-field dc analog of Shaka and Freeman's 180°,180°,180°, spatially selective pulse (8) are presented in Fig. 4. For comparison, high-field experiments, in which rf pulses are applied before demagnetization, are also shown. From the characteristic six line spectrum of a heteronuclear (13C-1H) spin pair in zero field (12), transitions corresponding to an initial zero-field state of \(-I_z + S_z\) are effectively produced with composite pulses.

These experiments illustrate simple applications of composite pulses, originally designed for high-field radiofrequency irradiation. Selective irradiation of isotopic species in zero field is a valuable asset in multiple-pulse experiments in zero field. A number of applications of these ideas in zero-field NMR is envisaged.

![Diagram](image)

**Fig. 4.** Spectra of \(^{13}\text{CHCl}_3\) (\(I = ^1\text{H}, S = ^{13}\text{C}\)) in an unaligned smectic B liquid crystalline phase with different zero-field initial conditions produced in high field and zero field. In (a) the characteristic seven line spectrum results with the initial condition equal to the equilibrium populations, \(4I_z + S_z\). A change in initial condition to \(I_z + S_z\) can be produced by applying a 75° pulse to \(I\) in high field as shown in (b). Similarly the populations of one spin species can be inverted relative to the other (\(-I_z + S_z\)) by applying a 105° pulse to \(I\) in high field before demagnetization. Zero-field analogs using composite dc pulses can also be used to selectively invert one spin species. The initial condition for (d-f) produced in high field before demagnetization is \(I_z + S_z\). In zero field only one spin is inverted before zero-field evolution with (d) a 180° \(^{13}\text{C}\) pulse (720° \(^1\text{H}\) pulse which leaves the protons unchanged; this is the simplest of composite zero-field pulses based only on the ratio of the magnetogyrnic ratios); (e) a narrowband 180° composite pulse (180°,180°,180°) applied to the protons; and (f) a narrowband composite pulse (180°,180°,180°) applied to the carbons. The resulting spectra all show the spectral frequencies indicative of an initial state proportional to \(-I_z + S_z\).
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