

A fast, stable quadrature phase generator for multiple-pulse NMR

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We present a fast quadrature phase generator for multiple pulse NMR experiments. The circuit maintains quadrature phase balance to 0.005° , and exhibits less than 0.03 dB of amplitude drift over a 24 hour period. The generator combines fine adjustability with a switching speed of 30 ns. It requires only a small number of rf components and can be made to operate over decade bandwidths.

INTRODUCTION

Modern NMR pulse sequences usually consist of a series of radiofrequency (rf) pulses having orthogonal (quadrature) phases. While there are a variety of situations where pulse accuracy is important,¹ it is especially critical for solid-state multiple-pulse NMR.² In fact, multiple pulse sequences developed for phase measurement exceed the accuracy of traditional electronic phase measurement techniques by an order of magnitude.³⁻⁵ Ease of phase adjustment and stability often determine whether or not an experiment is feasible. Such quadrature phase shifting circuits are often deficient in this respect, suffering from a variety of defects, including thermal drift, interchannel crosstalk, and coarse settability. We present a design in which these weaknesses have been removed or minimized and additionally, requires only a small number of rf components.

I. BACKGROUND

The most widely referenced designs for generating pulses with four variable amplitudes and phases are those of Vaughan⁶ and Waugh⁷ and Gerstein.⁸ All of the above designs start with four sources of continuous rf with independently adjustable amplitudes and phases. Each of these four signals are blocked by an rf switch and the outputs of the four switches are fed to a single port using a combiner. A pulse with the desired phase is selected by gating the appropriate switch.

The design described here is an adjustable version of the quadriphase modulator, a device which has been in existence for at least forty years, starting with the Armstrong modulator for FM transmission.^{9,10} In this design, an rf carrier is split into two orthogonal phases, each of which is amplitude and phase modulated using a mixer and dc control voltages. The modulated rf from each mixer is recombined to generate one rf signal having the desired phase and amplitude. Each rf phase is selected by driving the mixer pair with control voltage pulses. While designs using digital-to-analog converters to provide the dc levels are well known, the circuit presented here relies entirely on precision analog techniques to achieve high stability, fast switching, and very fine settability. The design uses high-speed analog switches to pass precisely reg-

ulated voltage levels to the mixer control ports in approximately 30 ns, with sufficient stability to maintain phases and amplitudes within 0.005° and 0.03 dB, respectively.

II. METHODS AND DESIGN CONSIDERATIONS

The quadriphase modulator is constructed using dc controlled double balanced mixers (DBMs), a quadrature splitter, and a two port combiner (as shown in Fig. 1). One of the mixers is biased by a dc control voltage at the IF port and rf at reference phase (i.e., 0°) is directed into the LO port. The second mixer is biased by an independent control voltage applied to its IF port, and rf, phase shifted by 90° with respect to the reference, is directed to its LO port. The outputs of both mixers are vectorially summed in the combiner. The phases of the 0° and 90° rf may be inverted by reversing the dc control voltages on the DBMs to produce

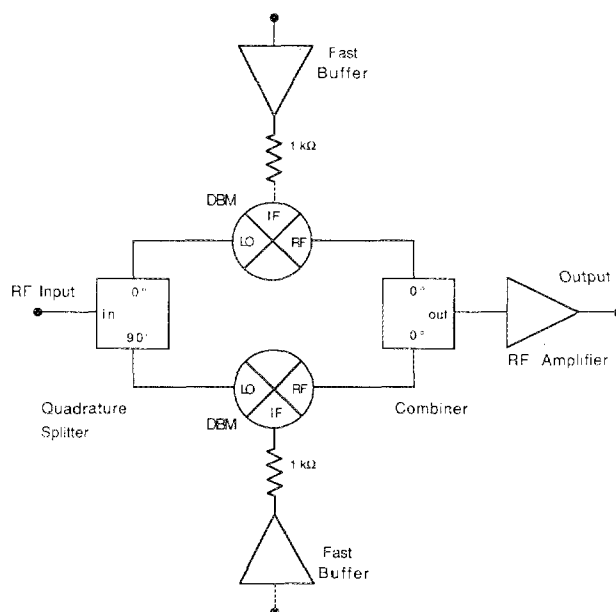


FIG. 1. An outline of a Quadriphase Modulator circuit, including the major radiofrequency components and fast mixer drivers. The double balanced mixers (DBMs) are shown with the rf entering through their local oscillator ports (LO). The control voltages are applied through the intermediate frequency (IF) ports and the attenuated rf is extracted from the radiofrequency (rf) ports. All components are connected using semi-rigid 50 Ω (UT-141, Microcoax Industries) cable and SMA connectors.

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180° and 270° rf phase shifts, respectively. The quadriphase modulator can therefore be used to generate four nominally orthogonal phase shifts, hence its name. In passing, quadriphase generation is usually performed in communications circuitry by driving both mixer IF ports fully positive or negative. These four combinations generate phase values of 45°, 135°, 225°, and 315°, and provide 3 dB greater amplitude than the scheme described here. The advantage of the current design is that phase and amplitude adjustments are nominally independent, since each is controlled by a separate dc level.

To adjust a particular choice of quadrature phase, the mixers are operated at reduced dc levels as voltage controlled attenuators. One of the mixers is driven strongly enough to provide the desired rf output level, while the other one is driven weakly to provide a lower rf level with a phase orthogonal to the first. When the two waves are vectorially summed as shown in Fig. 2, the amplitude of the weak, orthogonal component can be adjusted to set the phase. In this way, precise adjustment of the phases and amplitudes is carried out using straightforward dc level adjustments, and the QPM becomes a wideband, precision *adjustable*, quadrature phase generator. The rf bandwidth of the QPM depends primarily on the bandwidth of the quadrature hybrid used to generate the initial quadrature phases. This can be decade frequency ranges if desired (e.g., Merrimac QHM-7-126), since the moderate imperfections of ultra-broadband quadrature hybrids are easily correctable by this circuit. The remaining rf components impose no practical limitations. In our case for example, the ZLW-1 mixers and ZMSC-2-1 splitter have operating bandwidths of 0.5–500 MHz and 0.1–400 MHz, respectively.

The principal advantage of the QPM-based phase shifter is its ability to choose rapidly between four orthogonal phases. The time required for phase shifting is primarily determined by the analog switch turn-on times. Using commercially available fast analog switches (e.g., Harris Model HI-201HS) it is possible to select a new bias voltage in about 30 ns. The switching times for most diode mixers are on the

Principle of a Vector Modulator

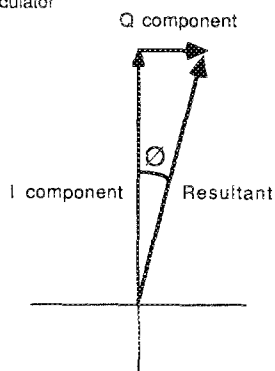


FIG. 2. The basic principle of the quadriphase modulation scheme used here. A large in-phase rf wave (I component) is combined with a weaker rf wave that is small in amplitude compared to I, and in quadrature with I. The I wave amplitude is adjusted directly, and the Q wave amplitude and sign are varied to alter the phase of the summed rf. These two adjustments are nominally independent when the phase corrections are small.

order of nanoseconds, and are not a limiting consideration. This fast switching speed also makes the mixers suitable substitutes for rf switches, since LO to rf port isolation is typically 40 dB.

This device is designed to produce square pulses for NMR experiments, which requires that the analog switches have settling times on the order of ten's of nanoseconds, with a minimum of interswitch leakage to avoid crosstalk. Another concern is small variation in switch resistance, since the on-state resistance weakly influences the mixer bias current. The switches must also be capable of handling a wide range of positive and negative dc voltages, as the drive current required will depend on the type of mixers used. Suitable devices include the Harris semiconductor HI-201HS and the Siliconix SD-5000 series switches. The HI-201HS switches were chosen for their fast turn-on time, ease of use, (they are packaged with integral drivers) and relatively constant on-state resistance. In order to achieve their rated turn-off times, the outputs of the switches should be connected to ground through a 1-k Ω resistor to allow the charge on the switch output capacitance to drain to ground. Smaller resistances will improve the fall time, but impose too great a current drain on the reference (LM-310) buffers over long pulse times. With more powerful buffers and smaller output resistors, the fall time will approach 20 ns. Since the outputs of the analog switches cannot provide enough current to properly bias the DBMs, they must also be buffered.

These voltage followers used to drive the mixers (referred to as the "fast buffers") must have a rise time equal to or better than that of the analog switches, or the high-speed performance of the circuit will be degraded. Ordinary voltage followers such as the LM-310 are not adequate. Suitable candidates include the National semiconductor LH0033 and LH0063, and the Harris HA-5002. All three have current gain at very high frequencies (past 90 MHz) and rise times on the order of <10 ns for the voltage ranges required. The LH0033 was chosen for this circuit based primarily on availability, but the HA-5002 would be expected to be equivalent. Any of the faster buffers, such as the LH0063, could be used in conjunction with an SD-5000 (Siliconix) analog switch if total switching times under 10 ns are required. Drive currents of 3–7 mA were used to bias Minicircuits ZLW-1 (+7 dBm LO maximum) DBMs. This was accomplished by placing a 1 k Ω current-limiting resistor between the output of the fast buffer and the mixer IF port, and using control voltages of three to seven volts (see Fig. 5).

The dc voltages are generated using temperature compensated Zener voltage references (analog devices AD-584KH). These references are buffered using voltage followers (National Semiconductor LM-310) to avoid loading effects and bypassed to ground using 0.1 μ F disk ceramic capacitors. The voltage followers were configured for extra negative current as specified in the device data sheet. The mixer control voltages are obtained by dividing the reference levels to the appropriate levels using internal divider networks, buffering these levels, and then passing them to front-panel mounted 10-turn potentiometers. Each quadrature channel has an amplitude and a phase adjustment potentiometer. The wiper voltages from the potentiometers range

Amplitude Control Voltages

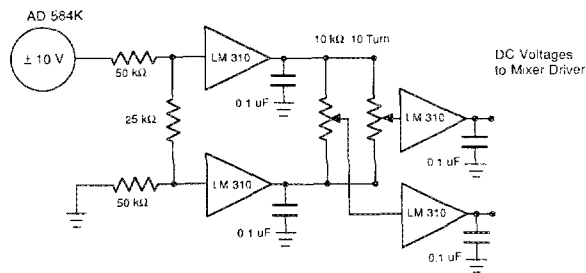


FIG. 3. The amplitudes of the major (in-phase) components of the phase-shifted rf are determined using a buffered voltage divider network with ± 3.34 to ± 6.67 V outputs. Positive voltages control the amplitudes for the reference and positive quadrature rf ($+90^\circ$ rf). The negative voltage ranges determine the amplitudes of the negative reference phase and the negative quadrature phases (180° rf and 270° rf, respectively). The dc voltages from the final LM 310 buffers are applied to the inputs of the analog switches of the mixer driver circuits. Capacitors and resistors are the same types as described for the mixer driver board (Fig. 5).

from 3.33 to 6.67 V for the 0° and 90° amplitude control voltages and -3.33 to -6.67 V for the 180° and 270° amplitude controls. All of the phase trimming voltages ranged from -0.5 to $+0.5$ V (refer to Fig. 3 and 4). The final buffered control voltages are routed to the inputs of the FET analog switches (see Fig. 5).

The stability of the quadrature phase shifts depends in part on the stability of the mixer control voltages. The primary voltage references can be regulated to ppm/ $^\circ\text{C}$ using off-the-shelf voltage references. The buffers following the references have offset drift specifications of approximately

Phase Control Voltages

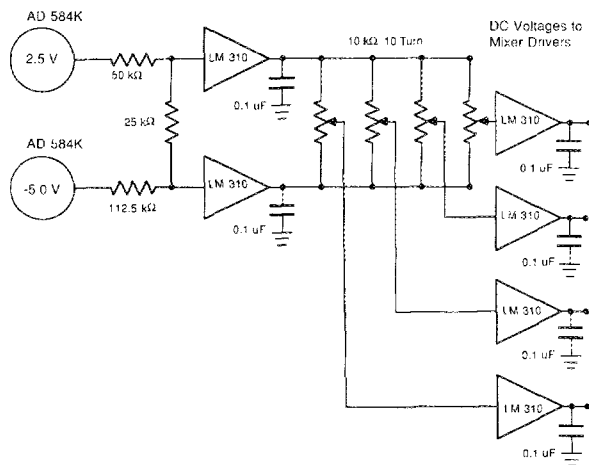


FIG. 4. The amplitudes of the small rf components (e.g., the Q component in Fig. 2) are controlled by a buffered divider network providing ± 0.5 V to the analog switches. The small components control the quadrature balance of the QPM, and are used to make the four channels orthogonal to each other. All resistors and capacitors are as specified for the mixer driver and amplitude circuitry (Figs. 3 and 5). The amplitude and phase control voltage sources are combined on a single PC board for compactness.

Mixer Driver Circuitry

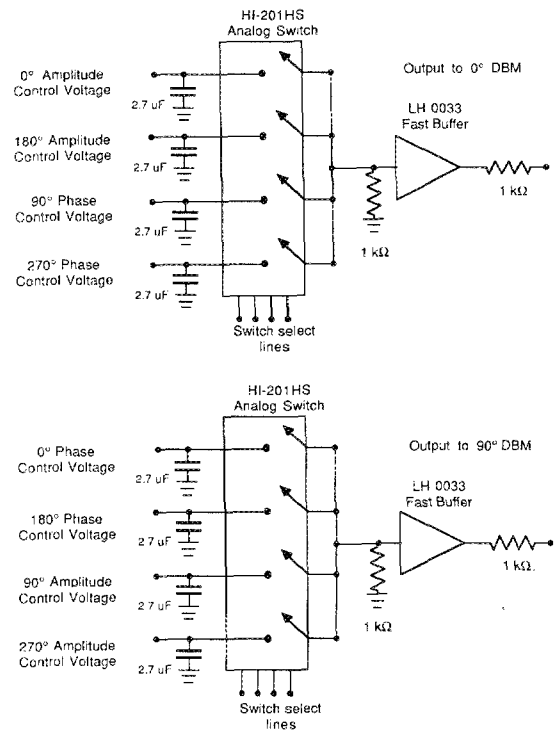


FIG. 5. The mixer driver circuitry is contained on a single, well-isolated PC board. The analog switch serves as an interface between the precise dc control voltages and the fast buffers used to drive the double balanced mixers. The $1\text{ k}\Omega$ resistor in parallel with the switch output allows the switch output capacitance to drain to ground after the switch is opened. The $1\text{ k}\Omega$ resistor after the LH 0033 buffer limits the current into the mixer IF ports. All resistors are metal film (1% tolerance) and all capacitors are 50 WVDC (Sprague) disk ceramic unpolarized capacitors.

10 ppm/ $^\circ\text{C}$ (for example the LM 310). The largest sources of thermal drift are the analog switches. The on-state resistance of the analog switches varies by $0.1\ \Omega/^\circ\text{C}$. Since the switch outputs are terminated in $1\text{-k}\Omega$ resistors, this translates to 100 ppm/ $^\circ\text{C}$ for the mixer bias current temperature coefficient. Though this represents a drift rate ninefold greater than that of the dc references, it is still within the tolerances required for millidegree phase stability. The mixer diodes are also subject to thermally induced changes in conductivity, but this has not proved to be an insurmountable problem. Mixers are not usually supplied with specifications for amplitude drift with temperature when dc biased through the IF port, but a series of improvised measurements using a biased mixer over a 25°C range (room temperature to ice) indicated a negative amplitude sensitivity ≤ 100 ppm/ $^\circ\text{C}$.

The phases and amplitudes are actually adjusted using ten-turn potentiometers. Although the ten-turn knobs are not entirely free of mechanical backlash, indirectly controlling the rf amplitudes and phases by means of dc voltages (analogous to "cold switching") has many advantages over mechanically actuated phase shifters and attenuators. Mechanical devices which depend on distance traversed along a screw thread or slide to effect a change in an electrical quantity are limited in their range and the fineness of their adjustments; fine increments over a large range are achieved only at great expense using precision vernier or micrometer con-

trols. Using electronic level controls, the range of the phase and amplitude adjustments can be varied over orders of magnitude without sacrificing precision just by changing a few resistors in a divider network. This feature is a necessary part of a phase shifter designed for an NMR spectrometer, where very small changes in rf phases are required to ensure proper functioning of pulse sequences (e.g., multiple-quantum NMR experiments^{4,11}).

The dc voltages are fed to the mixer drivers by selecting one of the four TTL inputs on each of the two analog switches (refer to Fig. 5). These can either be controlled from the spectrometer pulse programmer directly, or, if preferred, demultiplexed from two lines. A problem may arise here, since the signal delays for the channels may not be identical due to differences in layout or variations in the delay times of individual devices. Ideally, all four quadrature channels should have the same post-trigger delay times, so that the time delay for a rf pulse should be independent of the channel selected. For this particular design, device delays are synchronous to within nanoseconds and have caused no noticeable difficulties with even the most exacting multiple pulse experiments. Should such a problem be noticed, adjustable monostables (devices such as the 74LS121 or 74LS123, for example) can be placed in the TTL trigger lines for compensation.

SMA connectors and 50- Ω semi-rigid coaxial line were used to connect the final buffer, double balanced mixers, splitters, and combiners. The line's rigidity prevents phase changes due to vibrations, and its excellent isolation eliminates potential rf interference between channels and from external sources. The rf components were all purchased in connectorized aluminum boxes, with either SMA female connectors (Minicircuits Labs), or with BNC female connectors and BNC to SMA adapters.

The outputs from the mixers are combined in a 2-port, 0° splitter/combiner (Minicircuits Labs ZSC-2-1). Since hybrid splitters have only approximately 3 dB of isolation between the sum port and the inputs, a change in the termination of the circuit could reflect rf back into the splitter and mixers and ruin the amplitude and the phase balance of the device. If one anticipates frequent modifications of the output loading, it is prudent to buffer the output of the QPM with a rf amplifier that has excellent reverse isolation characteristics ($S_{12} \gg -40$ dB). This prevents the phase shifts delivered by the QPM from depending on the final combiner termination. The extra gain provided by such a final amplifier is also useful in that a QPM so equipped can usually drive a power amplifier directly. A simpler way to achieve termination independence is to guarantee a 50- Ω output impedance by the reverse strategy of using a terminating attenuator, albeit at the expense of signal level.

III. CONSTRUCTION AND LAYOUT

The dc portions of the circuit were constructed on double sided, copper clad printed circuit (PC) board. Since any transients or ringing on the mixer control pulses can cause phase or amplitude errors in the rf pulses produced by the QPM, care was taken to stabilize and/or isolate critical voltages. The dc circuitry was grouped into three separate boards; the first containing the dc voltage references and

buffers, the second the switches and high-speed buffers, and the third TTL circuitry for controlling the switches. Separating the precise, stable dc section from the fast mixer driving stages helps to maintain the stability of the reference sources by isolating them from switching transients which arise when rapidly changing the mixer bias voltages. To further isolate the fast components, the LH0033 buffers were placed inside rectangular boxes made of copper clad PC board with tight-fitting copper lids, which were thoroughly grounded. All power supply connections for the fast buffers were bypassed within a few millimeters of the devices on the circuit board, using 0.47- μ F ceramic and 5.6- μ F solid tantalum capacitors. All the resistors used in the QPM were low-inductance metal film types with less than 100 ppm thermal drift. The switches on the mixer driver board were isolated by a ground plane to prevent switching transients on the signal lines from being coupled through to the fast buffers. The switch outputs and TTL trigger inputs were placed on the opposite side of the copper-clad PC board from the dc control voltage lines. As complete a ground plane as possible shielded the dc side. The dc reference buffer outputs (the final LM 310 outputs in Figs. 3 and 4) were connected directly at the analog input pins of the switches and heavily stabilized with capacitors (0.47- and 2.25- μ F ceramic) directly from the pins to the ground plane. These precautions are imperative for ensuring fast settling of the QPM output.

One of the major advantages of the phase shifter presented here is the small number of parts it requires. All of the rf components used are relatively inexpensive and readily available in connectorized packages. A wide variety of buffers and voltage references can be substituted for the devices mentioned in the design section. The same is true for the double balanced mixers and rf splitters.

The use of printed circuit boards or equivalent high-frequency construction techniques is necessary for the fast mixer driver board, where the mixer control voltages have rise times on the order of tens of nanoseconds. If, however, fast settling is not mandatory, less rigorous layout techniques can be used. The remaining analog and TTL control circuitry can be wire-wrapped or constructed on vector board if the facilities for making PC boards are difficult to obtain. Standard (RG-58A/U or equivalent) coaxial line could probably be substituted for the semi-rigid coaxial transmission line (UT-141), although the resulting leakage and vibrational instability may compromise the stability and accuracy of the QPM.

IV. RESULTS

The QPM prototype described here was used to produce quadrature phase shifts for the 30-MHz intermediate frequency (IF) stage of a home-built 180 MHz proton NMR spectrometer. The phases and amplitudes of the four quadrature channels were set initially using a HP model 8405A vector voltmeter accurate to 0.1° and 0.2 dB⁵. After installation on the spectrometer (equipped with an ENI 5100L power amplifier), the amplitudes of the four channels were adjusted by observing the NMR response to a train of identical rf pulses^{11,12} applied to a liquid sample, which consisted of a 2-mm diam glass bulb filled with acetone doped with

0.001 M Cr(acac)₃ (II). The amplitude drift of the QPM can be estimated by observing the nutation rates for all four phases. High stability of the final mixing stage of the 180 MHz spectrometer and the final power amplifier, and good rf field homogeneity are crucial for assessing changes in rf amplitude. If all four drift together then any power fluctuations observed probably do not arise from the QPM. The upper limit on amplitude drift estimated from NMR experiments was 0.034 dB/day (see appendix A).

The phase stability of the QPM was measured by NMR as well, using specially designed pulse sequences which produce a nutation proportional to rf phase difference and eliminate effects due to pulse imperfections,^{3,4,13} such as phase transients,^{6,7,14} amplitude drift, and resonance offsets. No phase drift was observed, over a twenty-four hour period, although changes of 0.005° would have been readily detected. An upper bound for phase drift is therefore estimated by NMR results [a representative example is shown in Fig. 6(b)] to be $\leq 0.005^\circ/\text{h}$ (see appendix B). Adjusting the phase of each quadrature channel weakly affects the amplitude of each channel to some extent, as phase trimming entails combining additional (orthogonal) rf with the channel being trimmed. This change in amplitude is proportional to the secant of the phase angle ϕ [$A/A_0 \approx A_0 \sec(\phi)$; refer to Fig. 2]. Adjusting the phases, changes the amplitude by a minuscule amount for phase trimming in the range of $\pm 2.5^\circ$; for a 5° phase change the amplitude will change by 0.017 dB. These tests demonstrate that the QPM is stable enough for multiple pulse NMR experiments.

V. DISCUSSION

The ability to switch analog signals at sufficiently high speeds has made this design possible. Its principal advantages derive from the fact that all the level control is performed at low frequency. This allows highly accurate and stable adjustments, while minimizing interchannel crosstalk and external interference.

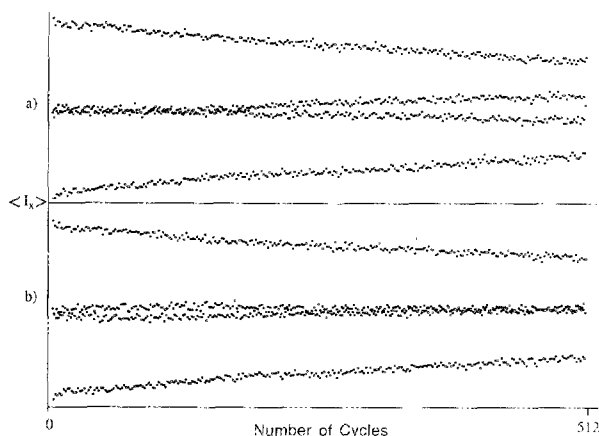


FIG. 6. Typical results of a phase measurement experiment when the rf phases are nominally in quadrature (b), and with an approximately 0.01° phase error between the in-phase and quadrature rf (a). The signals shown are the x component of the nuclear magnetization plotted against the number of NMR phase measuring cycles. Experimental conditions are: $S/N \approx 20$, 512 cycles and a cycle time of $170 \mu\text{s}$.

The QPM rf circuitry also has substantial advantages over more complicated switched quadrupole devices. Only one rf phase is present at any given time, so cross-channel interference is impossible. Additionally, the device is useful over a large rf bandwidth. Although the scheme presented here is intended for a 30-MHz operating frequency, the only frequency limiting component is the quadrature splitter at the front end of the QPM. Wider range quadrature splitters are available: devices covering decade bandwidths are available from suppliers such as Merrimac or Olektron. Two of the authors have constructed a similar unit at the Naval Research Laboratory (Washington, D.C.) for a homodyne spectrometer operating from 10 to 100 MHz. Adding a broadband quadrature hybrid at the receiver mixing section, permits multiple pulse experiments to be carried out over a large frequency bandwidth merely by resetting a synthesizer and changing the receiver preamplifier. Finally, the device can be constructed economically: the cost of parts for the device described here is approximately one thousand dollars.

ACKNOWLEDGMENTS

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APPENDIX A: rf AMPLITUDE STABILITY DETERMINATIONS

NMR can be used as a sensitive measure of rf amplitude or power. Consider the NMR response of the spins in a liquid sample to a train of identical rf pulses. Each pulse causes the bulk nuclear magnetization in the sample to nutate around the applied rf magnetic field by an angle θ per pulse. The nutation angle θ is directly proportional to the magnitude of B_1 , according to the relation $\theta = \gamma B_1 t_p$, where t_p is the pulse duration and γ is the nuclear gyromagnetic ratio. A train of such pulses therefore forces the magnetization to nutate around the rf field at a rate proportional to the angle θ per pulse, making the NMR response proportional to the rf magnetic field strength B_1 . The nutation rate is given by the pulse angle divided by the pulse time: $\omega_{\text{nutation}} = \theta_p/t_p$ radians/s. The magnetization is sampled in small "sampling windows" in between the pulses, during which the transmitter is gated off and the receiver is enabled.^{12,13} The sampling windows are far shorter than the periods of any of the natural frequencies of the spin system, and the rf magnetic fields are stronger than any of the local fields present (equivalently; $t_{\text{window}} \ll 2\pi/\omega_{\text{local}}$ and $\omega_{\text{nutation}} \gg \omega_{\text{local}}$). Under these conditions, the magnetization does not change appreciably over the sampling windows, and all of the nutation frequencies observed are due to rf induced precession. Since the rf field is not perfectly homogeneous across the sample, the signal will decay with a time constant approximated by the inverse of the bandwidth of nutation frequencies. The Fourier trans-

form of the rf nutation signal will have a linewidth and shape which reflects the distribution of rf magnetic field strengths acting on the sample.

The stability of the rf amplitudes can be estimated from the change in nutation rates over time, which corresponds to a shift in the line position. A conservative estimate of the minimum drift observable is a change of a single point in the transform. The change determined by this method depends on the digital resolution of the transform. The range of nutation frequencies sampled (the "sweep width") is determined by the pulse length (bandwidth = $1/t_p$). The bandwidth divided by the number of points is the digital resolution. For a pulse with nutation angle $\pi/2$ and a duration of 2.5 μ s, the nutation rate is 100 kHz and the transform bandwidth is 400 kHz. A 512 point transform will have a digital resolution of ≈ 782 Hz/point. This leads to an estimate of the amplitude drift:

$$(\omega_1^0 - \omega_1)/\omega_1^0 = (100 \text{ kHz} \pm 0.782 \text{ kHz})/100 \text{ kHz}.$$

The drift in decibels is $10 \log(1 \pm 0.00782) = \pm 0.034$ dB. Smaller changes in amplitude can be resolved, provided that a spectral shift of less than one point in the transform is observable. This is readily possible given adequate signal to noise. Note that the amplitude stability given by the rather drastic criterion of a one point shift is still too small to measure using commercially available rf instrumentation. The QPM circuit was stable to at least a single point drift over a 24-h observation period.

APPENDIX B: PHASE STABILITY

Radio-frequency phases can also be measured accurately using multiple pulse NMR. Pulse sequences are available which produce a rotation around a single axis which is proportional to the phase difference between pairs of the pulses.^{3,4} The spin magnetization precesses at an average rate which depends on the ratio of the phase difference to the cycle time, $\omega_\phi = \phi/t_c$, directly analogous to the amplitude measurements discussed in Appendix A. The pulse sequence used was that of Refs. 3 and 4, which produces a 2ϕ rotation for a difference of ϕ between two pairs of rf pulses. The sequences are compensated so as to be unaffected by common experimental imperfections such as resonance offsets, rf inhomogeneity, and phase transients. For an ensemble of isolated spin-1/2 nuclei initially in thermal equilibrium, the NMR signal after k such cycles is proportional to $\sin(2k\phi)$. The special case of pulses having orthogonal phases produces a 180° rotation per cycle, so exactly quadrature phased pulses produce no NMR signal [$\sin(k\pi) = 0$]. This null response can be used to indicate a perfect 90° phase shift. The accuracy of this method depends on the signal-to-noise ratio (S/N) of the NMR spectrometer system, as a null can only be determined to within the noise present in the time domain

signal. Since the response is proportional to $\sin(2k\phi)$, it is possible to estimate the error in the quadrature phases by measuring the signal intensity after k cycles of the pulse sequence have been applied. A phase error of ϵ will produce a signal equal to $A_0 \sin(k\pi + 2k\epsilon)$ at the k th cycle, where A_0 is the signal strength. The smallest change in the signal amplitude which can be resolved is equal to the noise N , so a phase error ϵ will be observable if

$$|A_0 \sin(k\pi + 2k\epsilon)| \geq N.$$

Noting that $|\sin(k\pi + 2k\epsilon)| = \sin(2k\epsilon)$, the error ϵ will be observed if it is larger than $1/\eta$, where $\eta = A_0/N$ is the signal to noise ratio.

$$\sin(2k\epsilon) \approx 1/\eta$$

$$\epsilon \approx 1/2k \arcsin(1/\eta).$$

For a S/N of 20:1 and 512 cycles, the smallest resolvable phase error is $\epsilon \approx 0.003^\circ$. An absence of any detectable signal after 512 points indicates that the phase error is less than 0.003° over the time of the experiment. A single 512 point transient was typically collected in 87 ms. The experiment was repeated once every two seconds for 12 h to measure the phase drift of the QPM. No drift was noted over a 10 h period, which gives an upper bound for phase drift of $\sim 3 \times 10^{-4}$ deg/h. No special measures were taken to control the ambient temperature (room temperature in the laboratory varied by approximately 1°C over this period), although care was taken not to cause any undue motion of the NMR apparatus during the course of the drift tests.

- ¹ G. A. Morris, *J. Magn. Reson.* **78**, 281 (1988).
- ² M. Mehring, *High Resolution NMR Spectroscopy in Solids*, (Springer, Berlin/Heidelberg/New York, 1976).
- ³ U. Haubenreiser and B. Schnabel, *J. Magn. Reson.* **35**, 175 (1979).
- ⁴ A. J. Shaka, D. N. Shykind, G. C. Chingas, and A. Pines, *J. Mag. Reson.* **80**, 96 (1988).
- ⁵ Hewlett-Packard Technical Manual for the HP 8405A Vector Voltmeter Hewlett-Packard Co., Palo Alto, CA (1977).
- ⁶ R. W. Vaughn, D. D. Elleman, L. M. Stacey, W. K. Rhim, and J. W. Lee, *Rev. Sci. Instrum.* **43**, 1356 (1972).
- ⁷ J. D. Ellet, M. G. Gibby, U. Haerberlen, L. M. Huber, M. Mehring, A. Pines, and J. S. Waugh, *Adv. Magn. Reson.* **5**, 117 (1971).
- ⁸ B. C. Gerstein, C. Chow, R. G. Pembleton, and R. C. Wilson, *J. Phys. Chem.*, **81**, 565 (1977).
- ⁹ Frederick E. Terman, *Electronic and Radio Engineering*, 4th ed. (McGraw-Hill, New York, 1955).
- ¹⁰ Samuel Seeley, *Vacuum Tube Circuits* (McGraw-Hill, New York, 1950).
- ¹¹ A. N. Garroway, *J. Magn. Reson.* **63**, 504 (1985).
- ¹² S. Idziak and U. Haerberlen, *J. Magn. Reson.* **50**, 281 (1982).
- ¹³ W. K. Rhim, D. D. Elleman, and R. W. Vaughn, *J. Chem. Phys.* **59**, 3740 (1973).
- ¹⁴ M. Mehring and J. S. Waugh, *Rev. Sci. Instrum.* **43**, 649 (1972).