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A new pulse generator for pulsed ESR

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Abstract. The construction of a new high-resolution multichannel low-cost pulse generator is reported. It is fully computer controlled through a simple RS232 serial interface. Its features are 1 ns resolution within any time, pulse delays up to 16 ms and pulse lengths up to 65 μs, and pulse sequence repetition rate from 66 Hz up to 250 kHz. It has fully programmable sequencing, including step increments for any pulse delay or length. It governs a Pulsed ESR spectrometer, which is also described, but it could be used in a very wide range of experimental set-ups. Finally, a few examples of spin–echo detected ESR and ESEEM of some paramagnetic centres are shown.

1. Introduction

Some high time–time resolution pulse generators have been described in the literature (see Quine *et al* 1987 and references therein), but we found that none of them fulfilled all our requirements. On the other hand, the use of high time resolution and accuracy delay circuits (Pesor and Lawrance 1990) would require too large a number of such devices. Furthermore, safety requirements specific to pulsed ESR (the need to protect sensitive detection devices against high signal intensities occurring during or shortly after excitation) could hardly be handled without much additional circuitry.

Several concepts have previously been applied for the design of multichannel high-resolution pulse generators:

(i) A fast memory (as wide as the number of channels required), flushing out its contents at highest rate (100 or 125 MHz). This straightforward solution has the advantage of easily realising complicated pulse sequences, but a very large amount of memory is necessary for long sequences. Furthermore time resolution is limited by the clock period, and changes in pulse set-up may be quite tedious.

(ii) An improvement to the first method consists in storing only state changes and durations of the next state in the fast memory, but it is still very difficult to have state duration shorter than memory read time.

(iii) A completely different approach consists in using delay generators. Long delay generators may be readily built by counting a high precision clock source. Short delays are usually achieved by comparing the level of a ramp generator with a programmed reference level. This method has the highest dynamic range (delays may range from 40 ps to milliseconds or seconds, depending on the width of the clock counter), but two delay generators are needed for each pulse.

We finally chose the method of delay generators, in a largely modular system, with pulses generated individually by independent and similar modules (called hereafter pulse units), and then linked to a channel by external circuitry.

2. Pulse generator design

2.1. Pulse unit

Each pulse unit produces one pulse within a sequence. Therefore as many pulse units as the total number of pulses in a whole sequence are required. Any pulse unit may be enabled or disabled. The delays are realised as follows:

(i) A high precision reference clock is counted with TTL counters to achieve long delays.

(ii) Fine delays are achieved by ECL delay generators (AD9500 Analog Devices). These are digitally controlled by an 8 bit word to produce up to 256 time steps of a delay time determined by an external RC circuit.

In our configuration, the frequency of the master clock is 4.0000 MHz and 250 time steps are used. Therefore, a final resolution of 1 ns is achieved, but with a 100 MHz clock, 40 ps time steps could be achieved with the same design.

The basic design of each pulse unit is shown in figure 1. The start signal is delayed by a first row of TTL counters. At the end of count (EOC), another row of TTL counters allows for long pulses. Fine pulse delay and fine pulse length are adjusted by ECL delay generators, which in turn control ECL flip-flops. The output of the first flip-flop is the pulse itself, and the output of the second one is a Ready signal. This one is set by the Start pulse itself, if the pulse unit has been enabled, and is reset at the end

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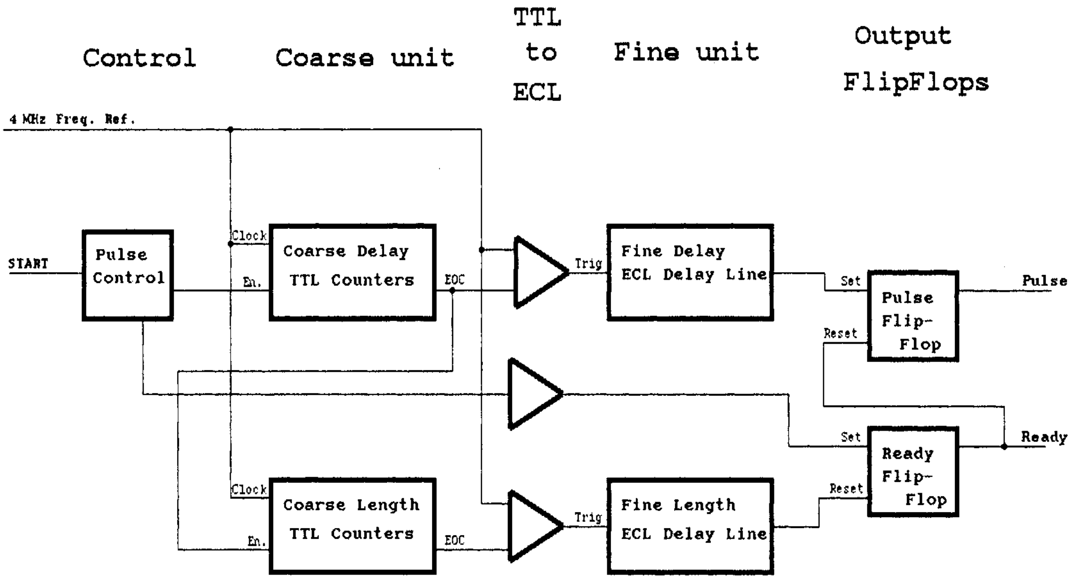

Figure 1. Schematic diagram of a pulse unit. The main circuits used are: 74LS592 TTL counters (2 for delay, 1 for length); 10H124 TTL to ECL converters; AD9500 ECL delay generators (Analog Devices); 10H131 ECL flip-flops. Microprocessor bus interface logic is not shown.

of the pulse. The pulse control flip-flop, the pulse delay and length counters and both fine delay generators are controlled by an external microprocessor.

2.2. External wiring

To form a multi-pulse sequence, one just has to link as many pulse unit outputs as necessary using the wired-or capability of ECL logic circuits. Similarly, the Ready outputs of the corresponding pulse units may be wired-ored together to give a control signal that will be set at the start of a pulse sequence, and will reset only with the end of the last pulse, whatever the number of enabled pulses and the delays or durations of any of them. In our system, this signal controls the shut-off of TWT residual noise and enables detection after a fixed delay.

2.3. Drivers

Drivers are needed to accommodate from ECL logic levels to specific device voltage and current requirements. PIN diodes are controlled through DH0035 PIN drivers (National Semiconductors). Another driver has been provided to control an RF switch for pulsed ENDOR experiments.

2.4. Overall control

A microprocessor based card controls all pulse units. Besides the RAM and EPROM memory, it contains an RS232 serial interface for external communication, allowing full control of the pulse generator system by any computer or terminal through a set of simple commands. Among the freely programmable parameters rank the sequence repetition rate, the number of sequences in a step, the number of steps in a scan, and the number of scan repetitions for S/N improvement. Furthermore, all pulse parameters, such as pulse delay and pulse length, are directly specified in nanoseconds, with an increment that is added after each step if needed. The master reference clock is also used as the microprocessor clock to avoid synchronisation problems. A counter–timer circuit controls the sequence time duration and the number of sequences in a step. At the end of each step, the microprocessor will compute new delay or length values, according to specified increments, and will reprogram the counters to new values. The system may be triggered externally or internally.

2.5. System performance

Time resolution for any pulse delay or length is 1 ns, according to our design. The maximum value for pulse delay or length then depends on the width of the respective TTL counters. In our system, we have 16 bit counters for the delay and 8 bit counters for the pulse length. This leads to a maximum delay of 16 ms and a largest pulse length of 65 μs. Sequence repetition rate may range from 66 Hz to 250 kHz. The number of identical sequences may range from 1 to 16000. Finally, the number of steps in a scan and the scan repetition number may reach 2^{16} (limited only by software).

As in all high bandwidth systems, great care should be applied to the physical layout, constant impedance lines, ground planes, power supply decoupling, etc. This has been found to be the greatest problem in the realisation of our pulse generator. In fact, short signal paths lead to high compactness, but also to higher stray capacitances. With our LeCroy 9420 digital storing oscilloscope (DSO), we measured an absolute accuracy of ± 1.5 ns on any signal, and a pulse to pulse time jitter of less than ± 0.5 ns on our generator.

3. Design of the pulsed ESR spectrometer

The schematic diagram of our pulsed ESR spectrometer is given in figure 2. The design is standard and requires only a few comments: PIN 1 shapes the microwave pulses before amplification. PIN 3 shuts off the residual signal and, importantly, at the same time the noise from the TWT amplifier. PIN 4 protects the microwave preamplifier and mixer from unwanted high intensity signals. PIN 2 produces microwave pulses at a lower level ($\leqslant 500$ mW).

Our 'Varian 9' magnet is controlled by a MarkII field dial, modified such that it can be computer controlled (Quine *et al* 1986) through an 18 bit D/A converter. An RF synthesiser (not shown in the figure) may also be used for CW or pulsed ENDOR operation. The output signal of the bridge is treated further either by a boxcar integrator followed by an A/D converter, or through our DSO with output already in digital form.

The computer governing the spectrometer is a Data-General DG30 desktop machine. The driving software is 95% written in Fortran 77. Only a few critical routines are in assembly language. This solution has the advantages of a high-level language combined with multitasking as well as real-time handling capabilities. More than 30 commands are available to the user. They allow full definition and set-up of all pulse parameters (including the possibility of easy parameter tuning), and to set up the magnetic field, RF frequency control and the scan progress control. They also allow data file handling and mathematical treatments such as exponential fits or fast fourier transforms.

The cavity used is a classical TE102 rectangular resonator. It is strongly overcoupled by an iris enlarged to ~8 mm, yielding a Q factor of ~300. Other cavity designs suited to our needs are under investigation.

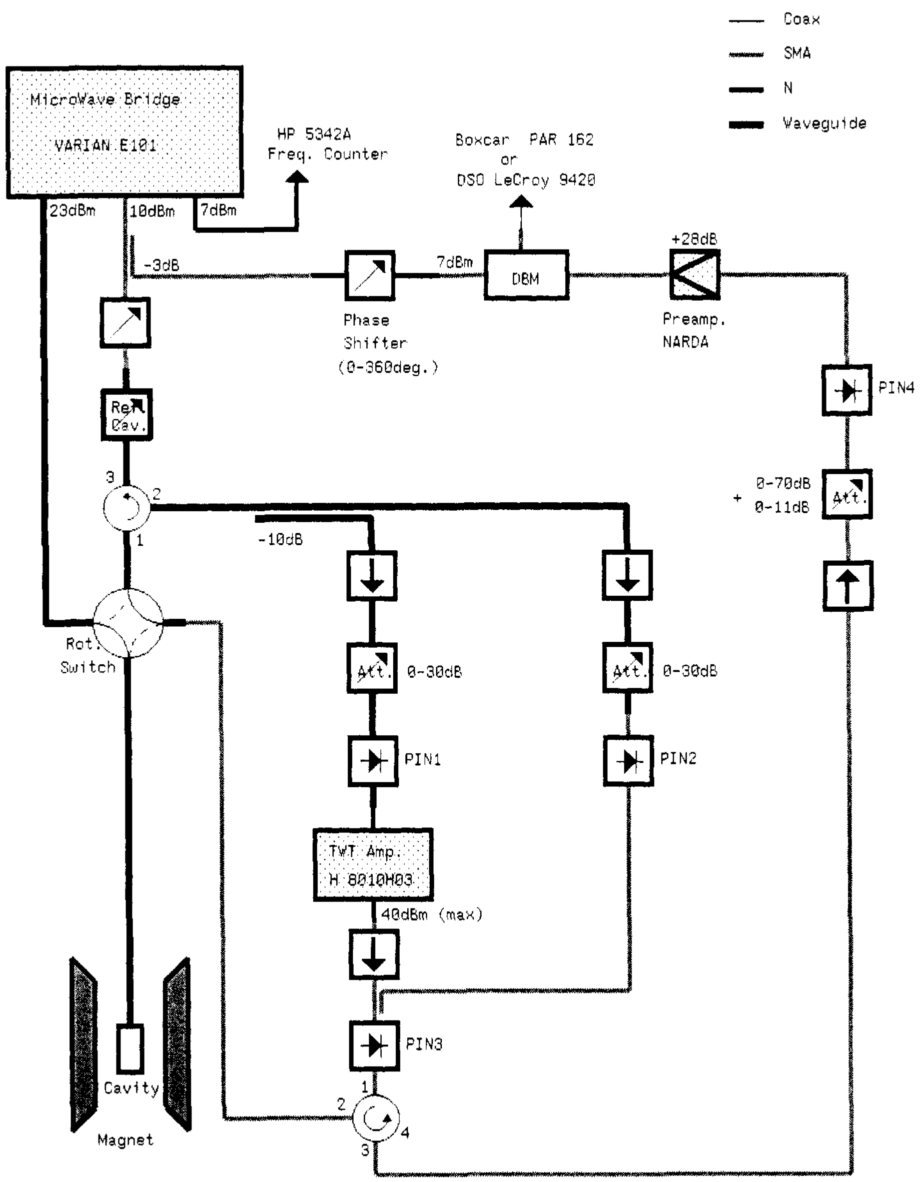

Figure 2. CW pulsed ESR spectrometer block diagram. The rotary switch is in CW position. Active circuits are: TWT Hughes 8010H03 (10W!); PIN 1 Microwave Associates MA-8319-1X17; PIN 2, 3, 4 Hewlett Packard HP33622A; phase shifter Narda Microline 3753B; Preamplifier Narda N6244S-237; doubly balanced mixer DBM Watkins–Johnson WJ-M14A.

4. Examples

We present here a few examples of the power and possibilities of our pulsed spectrometer. Its main limitation is currently the small output power of the TWT amplifier. The first centre we studied was the O_3^- molecule ion in natural yellow fluorites (Bill 1982). This centre was found to give a very strong echo from liquid helium temperature up to room temperature, with only a small decrease in relaxation times. Figure 3 shows the progress of a two-pulse experiment as seen by the DSO. Pulses are seen although the detection is off (in fact, 'off' means 80 dB attenuated). An initial delay of 83 ns is arbitrary. The experimental set-up consisted of a 60 ns $\pi/2$ pulse, then a 540 ns delay followed by a 120 ns π pulse. These values correspond quite well to the indicated measured ones, although signal build-up time in the cavity introduces some uncertainty in the measured values. The detection is switched on 300 ns after the last pulse. This gives the very sharp signal edge at 1100 ns, followed by the end of the signal due to cavity ringing. A very strong echo appears after $\tau + (\tau_{\pi/2} + \tau_\pi)/2$.

Figure 4 shows the angular variation of electron spin-echo detected ESR when the direction of the static magnetic field is swept from a C_2 to a C_4 crystal axis in a (110) plane.

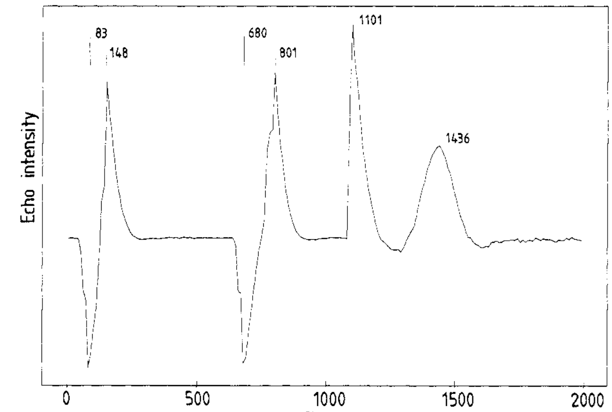

Figure 3. Spin–echo formation in O_3^- centre in calcium fluoride. Magnetic field $H = 0.3306$ T, parallel to C_3 crystal axis; microwave frequency = 9.4376 GHz; $T = 77$ K. The spectrum is the result of 1000 samples averaged in 8 s by the DSO. See text for explanations.

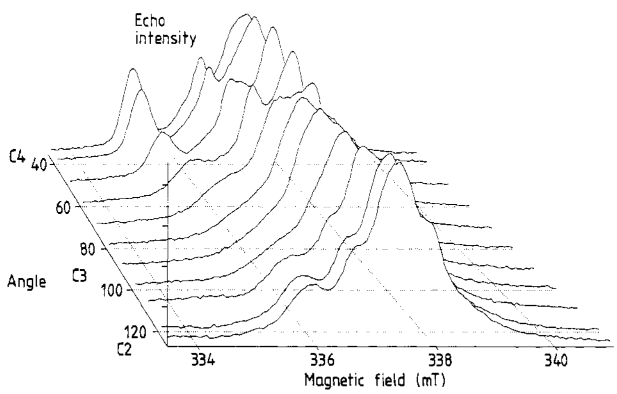

Figure 4. Spin–echo dependence against magnetic field intensity and angle for the same centre. Pulse sequence was: first pulse 60 ns; 540 ns delay; second pulse 120 ns. Microwave frequency = 9.4769 GHz; $T = 77$ K.

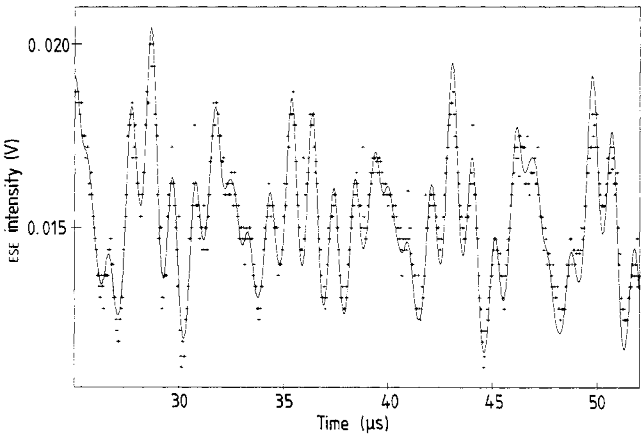

Figure 5. Three-pulse electron spin–echo envelope modulation (ESEEM) of $BaF_2{:}Ag^{2+}$. Conditions are: $H = 0.3005$ T, parallel to C_3 crystal axis; $T = 4.2$ K, microwave frequency = 9.3261 GHz. The symbols (+) denote experimental data points; the full curve is the best fit.

Figure 5 exhibits part of a three-pulse electron spin-echo envelope modulation (ESEEM) spectrum. The investigated centre is the Ag^{2+} ion in a BaF_2 crystal. This was shown to have very long relaxation times (Bill *et al.* 1989). The experimental data points are fitted with a three-pulse modulation formula (Mims 1972):

$$E(t, \tau) = \prod_i^n \left(1 - \frac{k_i}{4}(1 - \cos\omega_{i1} t)(1 - \cos\omega_{i2} t) \times (1 - \cos\omega_{i1}\tau)(1 - \cos\omega_{i2}\tau)\right).$$

Two pairs of slightly different nuclear hyperfine frequencies are found, due to both ^{107}Ag and ^{109}Ag isotopes. These are $\omega_{11} = 0.319$, $\omega_{12} = 1.044$ MHz and $\omega_{21} = 0.280$, $\omega_{22} = 0.907$ MHz. Further investigations are underway and complete results will be given elsewhere.

5. Conclusions

We have presented the design of our new pulsed ESR spectrometer. The heart of the spectrometer is the new pulse generator. Its modular conception and construction allows very easy applications and extensions in the fast moving field of time-domain experiments. The two output signals per pulse unit make safety requirements very easy to fulfil, and allow generation of useful secondary signals. New pulse units may be added to trigger nearly any kind of external device.

Acknowledgment

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