V-O Development of Broadband Solid-State NMR Spectroscopy

There are two different fields of solid-state NMR. One is biological, chemical and polymer NMR and the other is magnetic or metallic NMR. The former NMR employs resonant-type NMR probes, which can be tuned only over bandwidth of a few 100 kHz. Nuclear spins are controlled very precisely by sculpted RF pulse sequences. The unambiguous assignments of the lines are possible by using chemical shifts and spin-spin or dipolar couplings. One big outcome is that NMR teaches us not only a local information of an observed nucleus, but also correlations between different nuclei. The NMR parameters offered challenging problems for quantum chemical calculations and are now well predictable. The commercialization promoted rapid developments of sophisticated instruments with high resolution and sensitivity and the developments seems to be almost completed. However, in magnetic or metallic samples, most NMR works have been focused on only local information, like Knight shifts, hyperfine couplings, and relaxation times. Two-dimensional correlation NMR seems to be unpopular for these samples.

In magnetic and metallic samples, usually resonance lines are much broader than the diamagnetic samples. Ordinary resonant type NMR probes have a narrow tuning range and are inconvenient. It is possible to observe the spectra by a magnetic field sweep and with a fixed carrier frequency. However, sometimes the magnetic properties depend on the strength of static magnetic field. For example, the chemical shift of conducting samples can be field dependent due to the de Haas-van Alphen Effect (more generally Aharonov-Bohm effect).[1),2)] We may also need a broadband NMR probe for frequency sweep experiments for studying such a subject. For ferromagnetic samples, the sensitivity of NMR is enhanced because motions of nuclear spins are coupled with motions of a macroscopic magnetization or domain walls. Detuned coils have been often used in a frequency sweep spectrometer. However, if the sensitivity is optimized, it may be possible to observe small patterned films, where various domain structures were theoretically investigated.

Here we reexamined a transmission line NMR probe, which was proposed by Lowe and coworkers in 70s.[3),4)] The probe is expected to work in a wide frequency range below a certain cut-off frequency. The circuit resembles to that of a low-pass filter, which consists of π sections with a coil and two capacitors. The characteristic impedance must be adjusted to cable impedance by choosing an appropriate capacitance value. Some numerical results have been described in a previous report. We extended the numerical works from flat transmission coils to cylindrical transmission coils, since the latter form was easier to produce by using tip capacitors.

When we have a broadband NMR probe, we also need a broadband RF generator. Adiabatic pulses may be very effective for this purpose. Other types of selective RF pulses may be also useful, when we excite only a part of a spectral region. Conventional rectangular pulses are inconvenient, since its excitation envelope extends over a wide frequency range. Pulse shaping is commonly employed in a solution state spectrometer. However, for solid samples, the modulation must be much faster than the solution. Even in many high-resolution solid state NMR works, a phase transient due to a fast RF switching have been ignored. Using a fast RF modulator can solve these problems and fast modulated RF pulses. It would be also an attractive subject how various forbidden transitions can be controlled by shaped RF pulses.

References
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V-O-1 Numerical Simulations and Experiments on the Transmission Line Probe

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Previously, we have reported the numerical simulations of flat transmission line coils. We extended the simulation to cylindrical transmission line coils and constructed NMR probes by using the cylindrical coils. Lowe and co-workers mentioned that flat coils have advantages of the construction and the RF field homogeneity. However, our numerical result showed the homogeneity of a cylindrical coil was comparable to that of a flat coil. The homogeneity was mainly caused by the reflections of RF at the both ends of the coil, where the characteristic impedance was different from the value at the coil center. The RF field strength decreases as the carrier frequency increases, because there is a phase delay between neighboring coil sections. The characteristic decay frequency is given by

$$\nu_d^{\text{cylinder}} = \left(Z_0 / \pi^2 \mu_0 a\right)\left(p/a\right)^2$$

where Z_0, p, and a are a characteristic impedance, a pitch, and a diameter of the coil. The resonance frequency of the observed nuclei must be smaller than ν_d^{cylinder}. This condition restricts the size of the coil. We wound coils with the size a = 2.3 mm and p = 1.2 mm. At first, we made probes with Z_0 = 50 Ω. The RF field strength at 400 MHz (^{1}H) was determined to be 60 kHz in experiments and was calculated to be 40 kHz for an input RF power of 100 W. However, the RF field strength of the ^{23}Na experiments at 106 MHz was found much weaker (11 kHz) both in the experiments and in the calculation. The RF field strength was improved by twice when Z_0 was decreased to 12.5 Ω and $\lambda/4$ cable impedance transformers were inserted at both the input and the output ports. The bandwidth was reduced to 30 MHz if $\lambda/4$ cable transformers were used. It is still much larger than the bandwidth of the ordinary resonant probe.

There are still some rooms for a further implementation. Noise of NMR signals is determined by resistive components in a probe circuit. In a transmission line probe, one port of the probe is terminated by a load or a transmitter (or a receiver). RF switches connect and disconnect them. The noise may be mainly generated at the load. If the load is cooled or resistance at load is reduced by appropriate impedance transformations, the signal to noise ratio might be improved. An ideal load must generate no thermal noise and absorb the signal completely. It may be also attractive to use a superconductor for the NMR probe circuit. One big problem of superconducting NMR probes (mainly used MRI) is that the probe Q becomes too high. The bandwidth of the probe is typically about 40 kHz, which allows only the observation of solution-state ^{1}H signals. The transmission line probe has a fast recovery time as a coaxial cable if the impedance is properly matched with the feeding and the receiving cables. More flexible design of superconducting probes may be possible by using transmission lines.

V-O-2 Developments of Fast Digital RF Frequency Modulator

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We used a quadrature digital upconverter AD9857 (Analog Devices). This IC generates the carrier signals and mixes them with the modulation signals digitally, so that the modulated RF output (f0 + fm) is expected to be free from the leakage of the carrier frequency signals (f0) and the counter-quadrature signals (f0 – fm), which are unavoidable in analog modulators. We added a memory module for supplying digital amplitude data to AD9857. The memory module contains a large SRAM (256k words) and small SRAMs (2k words) for storing series of shaped pulses, starting addresses, and numbers of data in a shaped pulse, respectively. The memory module is controlled by three external TTL signals. It can be used in either a single pulse mode or a CW mode. In the latter mode, a shaped pulse is repeated until the external TTL signal is turned to high. The other TTL signals are employed to initialize the start address and to trigger pulsing. For the details of the design, please contact with Mr. Yoshida in Equipment Development Center. Some fast ICs were only available in a TSSOP package (lead pitch 0.65 mm). Mr. Yoshida did quite elaborate soldering works. Although commercial fast function generators are available, it is quite expensive and is not so convenient for magnetic resonance experiments. It may also have some pedagogical merit to know the actual design of the modulator, since the RF modulation is commonly used in communication technologies, and is a prototype of optical communication technologies. If there are several users who are interested in our fast digital RF modulator, it may be possible to order a company, who has a soldering machine, to make the printed circuit boards.