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Ringing effects eliminated spin echo in solids

Chao Ma [a,b,1], Peng Li [a,1], Qun Chen [a,*], Shanmin Zhang [a,*]

[a] Department of Physics, Shanghai Key Laboratory of Magnetic Resonance, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, PR China
[b] Department of Radiology, Changhai Hospital, The Second Military Medical University, 168 Changhai Road, Shanghai 200433, PR China

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ABSTRACT

Two types of ringing effects eliminated spin echo sequences have been introduced. To achieve the task, two additional 90° pulses with proper phase cycles are placed at the beginning of the pulse sequences. The spin echo time is calculated with the perturbation method to the first order, i.e. taking into account only the dipolar secular term. The non-secular term causes an imaginary part of the FID, leading to an unsymmetrical NMR spectrum. This effect, according to a symmetry of NMR sequences under phase inversion, can be compensated by inverting all the x and $-x$ or y and $-y$ phases. The properties of the symmetry are derived based on the theory of density matrix. In addition, the non-secular term also results in a small drop (several per cent) of the echo amplitude, but it nearly does not affect the echo time. With these pulse sequences we are able to get a spectrum with an echo delay only 1.1 μs without distortion using a Bruker AVANCE III NMR instrument.

1. Introduction

Spin echo in liquids was discovered by Hahn in 1950 [1], where the chemical shifts were refocused by a 180° RF pulse and a spin echo was formed at the end of the pulse sequence. This idea was soon adapted in solids to refocus the dipolar interaction, such as in the solid echo [2–4], WHH type sequences [5–7], magic echo [8], and polarization echo [9]. In general, a spin echo will form as long as the dipolar interaction is inverted or averaged to zero over a period of time. These echo sequences have been successively used to avoid dead-time problem of an NMR receiver, remove the effects of dipolar interaction [5–7], test the spin temperature hypothesis [8,10], reveal the time reversal of spin diffusion in solids [9], etc.

It is often necessary to derive an echo with a very short delay time (several μs) in order to avoid additional decay of the echo amplitude [11] or to get quantitative information in the analysis of various molecular compositions [12]. This requires a preamplifier with a very short dead-time, which, according to the general opinion, is a great challenge even to a modern NMR instrument.

According to our experience, the ringing effects cause a severe distortion of the NMR spectra for short delays. However, it has been shown [13] that the ringing signals can be effectively removed with proper phase cycles of the RF pulses if they do not saturate the preamplifier. This scheme is adopted for use in the spin echo sequences. The real dead-time can be much smaller than expected by eliminating the ringing effects. With a Bruker AVANCE III NMR instrument we were able to get an echo with nearly no distortion for a delay time only 1.1 μs, the shortest time allowed in order to protect the instrument.

The echo time is calculated based on the perturbation method combined with the average Hamiltonian theory as shown in the calculation of the windowless solid echo [4]. In the calculation, the non-secular term of the dipolar integration is discarded while the secular term remains. Since the secular term commutes with the spin-locking term, it significantly simplifies the calculation. Moreover, the result is remarkably accurate under the strong pulse conditions as demonstrated by a homemade Java program called quantum computation of nuclear magnetic resonance (QCNMR).

The dipolar non-secular term in the presence of the RF pulses may make a noticeable contribution to the imaginary part of the FID, leading to an unsymmetrical NMR spectrum. To eliminate these effects, either all the RF pulses with x and $-x$ or y and $-y$ phases need to be phase inverted in every other scan, which results in a negative imaginary or real part of the FID. The unsymmetrical NMR spectrum can be corrected by adding or subtracting the two consecutive FIDs. This scheme of phase inversion, which just changes the sign of the imaginary or real part of the FID but not their magnitudes, follows a symmetry of NMR sequences under phase inversion, which will be discussed in detail.

2. Elimination of the ringing effects

For a tuned probe circuit, each RF pulse produces a damped signal (ringing) of the same frequency as the RF pulse [11–14]. The ringing effects become stronger if the probe quality factor (Q) is

* Corresponding authors.
E-mail addresses: qchen@admin.ecnu.edu.cn (Q. Chen), shanminz@hotmail.com (S. Zhang).
[1] These authors contributed equally to this work.

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larger. As long as the preamplifier is not saturated, these ringing signals will linearly superimpose when multiple pulses are applied.

To eliminate the ringing effects of each individual RF pulse, the same phase of the pulse must appear at least twice with opposite receiver phases, one with a positive ringing signal and the other a negative one [13]. Unlike the ringing, the NMR signal follows the rules of quantum mechanics. For example, a single 180° pulse will invert the magnetization but not the ringing. Therefore, by properly inserting a 180° pulse and arranging the phases of the pulses and receiver, the ringing effects can be effectively eliminated as shown previously [13]. This simple scheme is adopted here for use with the spin echo in solids.

The phases for a ringing effects eliminated spin echo (REESE) with four 90° pulses (Fig. 1a) are shown in Table 1, where a 180° pulse is formed when the first two pulses have the same phase y or $-y$. It can be seen that for each pulse phase there is always two receiver phases, one positive and the other negative. The relative polarity of each ringing is also denoted in Table 1. By running four (or eight) scans with different combination of phases, all the ringing effects are eliminated while the NMR signals are accumulated four (or eight) times as shown in Table 1.

3. Calculation of spin echo with the perturbation method

According to the perturbation theory of quantum mechanics [15], in the presence of strong RF fields only the dipolar secular term needs to be considered to the first-order. During spin-locking time, the non-secular term has no accumulative effects because for each duration of 180° pulse it averages to zero. Besides the effects of the non-secular term is one magnitude smaller than the secular term, therefore it is eligible to be discarded especially under strong pulse condition. As we show in the following the non-secular term leads to a slight asymmetry of the spectra, but it will not affect the echo peak time. Since the secular term $\mathcal{H}_{dsec}$ commutes with the RF term, the calculation is simplified considerably [4]. As an example, we calculate the pulse sequence shown in Fig. 1a with the phases $\theta_1 = y$, $\theta_2 = -y$, $\theta_3 = y$, $\theta_4 = x$ and the receiver phase x. The propagator at the end of τ' can be expressed as

$$P(\tau'_{end}) = e^{-i\mathcal{H}_{dz}\tau'} e^{-i\left(\omega_1 I_x - \frac{1}{2}\mathcal{H}_{dx}\right)pw} e^{-i\mathcal{H}_{dz}\tau} e^{-i\left(\omega_1 I_y - \frac{1}{2}\mathcal{H}_{dy}\right)pw} e^{-i\left(-\omega_1 I_y - \frac{1}{2}\mathcal{H}_{dy}\right)pw} e^{-i\left(\omega_1 I_y - \frac{1}{2}\mathcal{H}_{dy}\right)pw} \tag{1}$$

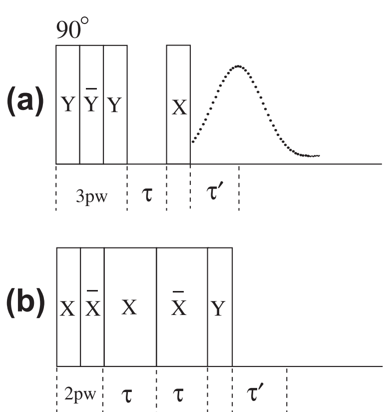

Fig. 1. Pulse sequences for ringing effects eliminated spin echo in solids. (a) A solid echo sequence preceded by two additional 90° pulse with two different schemes of phase cycles: $y, -y, y, x, x$; $y, -y, -y, -x, -x$; $-y, -y, -y, -x, x$; $-y, -y, y, x, -x$; $y, -y, y, -x, x$; $y, -y, -y, x, -x$; $-y, -y, -y, x, x$; $-y, -y, y, -x, -x$, and $x, -x, y, x, x$; $x, x, y, x, -x$; $x, -x, -y, x, -x$; $x, x, -y, x, x, -x, x, y, -x, x$; $-x, -x, y, -x, -x$; $-x, x, -y, -x, -x$; $-x, -x, -y, -x, x$. To the former scheme the echo appears at $\tau' = \tau + 3pw/2$ and to the later $\tau' = \tau - pw/2$. (b) A windowless solid echo preceded by two additional 90° pulses, which requires a phase cycle of $x, -x, x, -x, y, x$; $x, x, x, -x, y, -x$; $-x, x, x, -x, y, x$; $-x, -x, x, -x, y, -x$; $x, -x, x, -x, -y, -x$; $x, x, x, -x, -y, x$; $-x, x, x, -x, -y, -x$; $-x, x, -x, -y, x$, and the echo appears at $\tau' = \tau + pw/2$.

where $\mathcal{H}_{dz} = \sum_{i<j} d_{ij}(3cos^2\theta_{ij} - 1)(3I_{iz}I_{jz} - I_i \cdot I_j)$ is the truncated dipolar Hamiltonian in the rotating frame and $-\frac{1}{2}\mathcal{H}_{dx} = -\frac{1}{2}\sum_{i<j} d_{ij}(3cos^2\theta_{ij} - 1)(3I_{ix}I_{jx} - I_i \cdot I_j)$, $-\frac{1}{2}\mathcal{H}_{dy} = -\frac{1}{2}\sum_{i<j} d_{ij}(3cos^2\theta_{ij} - 1)(3I_{iy}I_{jy} - I_i \cdot I_j)$ are the secular terms of $\omega_1 I_x$ and $\omega_1 I_y$ respectively. Since $\omega_1 I_x$ and $\omega_1 I_y$ commute with their secular terms $\mathcal{H}_{dx}$ and $\mathcal{H}_{dy}$ respectively, the propagator in Eq. (1) can be rewritten as

$$\begin{aligned} P(\tau'_{end}) &= e^{-i\mathcal{H}_{dz}\tau'} e^{-i\omega_1 I_x pw} e^{-i\left(-\frac{1}{2}\mathcal{H}_{dx}\right)pw} e^{-i\mathcal{H}_{dz}\tau} e^{-i\left(-\frac{3}{2}\mathcal{H}_{dy}\right)pw} e^{-i\left(\omega_1 I_y\right)pw} \\ &= e^{-i\omega_1 I_x pw} e^{i\omega_1 I_x pw} e^{-i\mathcal{H}_{dz}\tau'} e^{-i\omega_1 I_x pw} e^{-i\left(-\frac{1}{2}\mathcal{H}_{dx}\right)pw} e^{-i\mathcal{H}_{dz}\tau} e^{-i\left(-\frac{3}{2}\mathcal{H}_{dy}\right)pw} e^{-i(\omega_1 I_y)pw} \\ &= e^{-i\omega_1 I_x pw} e^{-i\mathcal{H}_{dy}\tau'} e^{-i\left(-\frac{1}{2}\mathcal{H}_{dx}\right)pw} e^{-i\mathcal{H}_{dz}\tau} e^{-i\left(-\frac{3}{2}\mathcal{H}_{dy}\right)pw} e^{-i\left(\omega_1 I_y\right)pw}. \end{aligned} \tag{2}$$

In the above calculation, a unit operator $e^{-i\omega_1 I_x pw} e^{i\omega_1 I_x pw}$ is inserted to perform a rotation of $\mathcal{H}_{dz}$ around the $-I_x$ axis. The propagator can be further simplified using the zero-order Average Hamiltonian [16,17],

$$\begin{aligned} \overline{\mathcal{H}}^0 &= \left(\mathcal{H}_{dy}\tau' - \mathcal{H}_{dx}\frac{pw}{2} + \mathcal{H}_{dz}\tau - \mathcal{H}_{dy}\frac{3pw}{2}\right) \\ &= \left[\mathcal{H}_{dy}(\tau' - pw) + \mathcal{H}_{dz}\left(\tau + \frac{pw}{2}\right)\right] \\ &= \left[-\mathcal{H}_{dx}\left(\tau - \frac{pw}{2}\right)\right] \quad for \quad \tau' = \tau + \frac{3}{2}pw. \end{aligned} \tag{3}$$

where the formula $\mathcal{H}_{dx} + \mathcal{H}_{dy} + \mathcal{H}_{dz} = 0$ has been used. Considering only the zero-order average Hamiltonian the propagator becomes

$$P(\tau'_{end}) = e^{-i\frac{\pi}{2}I_x} e^{i\mathcal{H}_{dx}\left(\tau - \frac{pw}{2}\right)} e^{-i\frac{\pi}{2}I_y}. \tag{4}$$

The density matrix at the end of τ' is

$$\begin{aligned} \rho(\tau'_{end}) &= P(\tau'_{end})\rho(0)P^{-1}(\tau'_{end}) \\ &\propto e^{-i\frac{\pi}{2}I_x} e^{i\mathcal{H}_{dx}\left(\tau - \frac{pw}{2}\right)} e^{-i\frac{\pi}{2}I_y} I_z e^{i\frac{\pi}{2}I_y} e^{-i\mathcal{H}_{dx}\left(\tau - \frac{pw}{2}\right)} e^{i\frac{\pi}{2}I_x} \\ &= e^{-i\frac{\pi}{2}I_x} e^{i\mathcal{H}_{dx}\left(\tau - \frac{pw}{2}\right)} I_x e^{-i\mathcal{H}_{dx}\left(\tau - \frac{pw}{2}\right)} e^{-i\frac{\pi}{2}I_x} \\ &= I_x. \end{aligned} \tag{5}$$

Even though $\overline{\mathcal{H}}^0$ is not equal to zero but it commutes with the density matrix I_x. It has no effects on $\rho(\tau'_{end})$ as if the initial density matrix $\rho(0) \propto I_z$ received nothing (to the end of τ') except an ideal $90°_y$ pulse. As a result, an echo forms at the end of $\tau'(=\tau + 3pw/2)$. In a similar way, it can be shown that the echo occurs at $\tau' = \tau - pw/2$ for the same pulse sequence but with different phase, $\theta_1 = x$, $\theta_2 = -x$, $\theta_3 = y$, $\theta_4 = x$. And, for the windowless solid echo (Fig. 1b) the echo occurs at $\tau' = \tau + pw/2$.

When $\tau = 0$, the echo occurs at $\tau' = pw/2$ for the windowless solid echo, which is the shortest echo sequence with elimination of the ringing effects. For a $pw = 2$ μs (90° pulsewidth), the echo occurs at $\tau' = 1$ μs, which exerts a strong demanding on the deadtime of the NMR hardware. The corresponding experiment is performed on a Bruker AVANCE III instrument with a digital receiver. As shown in the experimental section, the results are remarkable.

4. The effects of the non-secular terms and their compensation

In the above calculation, the non-secular term has been completely ignored. It is valid for extremely strong RF pulses. For a RF field strength $f_1 = 125$ kHz (or $pw = 2$ μs), the strong pulse condition is not quite fulfilled regarding to a dipolar interaction with a coupling constant $d = 26.8$ kHz or so. It has been shown by computer simulation with a pair of dipolar coupled spin-1/2 system that the non-secular term introduces an imaginary part of the FID up to 14.3% of the echo amplitude. It also reduces 2–3% of the echo amplitude. However, as a miracle the non-secular term has almost no effect on the echo time. Therefore, it is very accurate to calculate spin echo time with the perturbation method.

In the following, the pulse sequence shown in Fig. 1a is used in the computer simulation with a delay time of $\tau = 2$ μs and echo