3 Spin Echoes and Carr Purcell

Among the multiple-pulse techniques for the investigation of quadrupole nuclei in powders, the two-pulse spin-echo methods are the oldest and are still widely used. Echo techniques provide two data sets in the NMR time domain. First, the echo decay is dependent on $t_2 - t_1$, which starts at the time $t_2 = t_1$ when the echo reaches its maximum; see Fig. 3.1. It gives similar information to the initial free induction decay after the preparation pulse, but the loss of signal during the ring-down of the probe and the recovery of the receiver immediately after the pulse are overcome. Second, by varying the pulse distance t_1 between the preparation pulse and the refocusing second pulse, the resulting envelope of the echo decay gives additional information about the spin system. The refocusing effect of a second pulse after a preceding $\pi/2$ pulse for an interaction that is proportional to I_z is called the Hahn echo. The original experiment by Hahn [1] was performed with identical-phase incoherent $\pi/2$ pulses in an inhomogeneous external magnetic field. The term "Hahn echo" is now used for the spin-echo after $\pi/2 - t_1 - \pi - t_1$ of spin-1/2 nuclei and also of quadrupolar nuclei with half-integer spins, if the central transition is selectively excited.

However, the quadrupole interaction strongly influences the formation of an echo: homonuclear dipolar interactions which mainly cause the decay of the spin-echo amplitude become less effective since spin-flipping between different transitions is forbidden. Due to the nature of the quadrupole coupling, which has first-order proportionality to I_z^2, refocussing is not complete. Also, the limited range of excitation for very broad lines of powder samples causes complicated spin-echo behaviors.

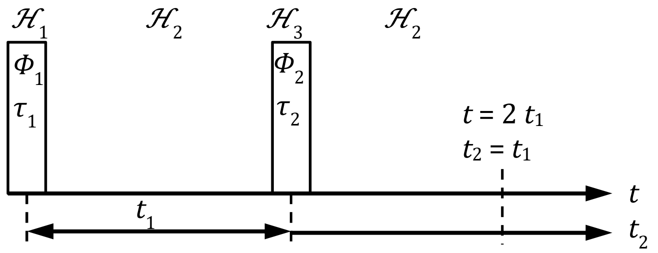

Fig. 3.1. Sketch of the two-pulse experiment. $\mathcal{H}_{1,2,3}$ represents the Hamiltonians in the interaction representation, where $\Phi_{1,2}$ and $\tau_{1,2}$ are the phases and durations of the two pulses, respectively.

3.1 Echo Studies

The majority of the previous echo studies on quadrupole nuclei used nonselective excitation and did not involve powdered substances. Das and Saha [2] calculated the echo response of nuclei experiencing first-order quadrupole interactions to a sequence of two pulses of identical duration and phase, neglecting dipole interactions. Solomon [3] showed that, when quadrupole interactions cause significant evolution of the spin system during the pulses, forbidden echoes occur which are not bell-shaped curves like the allowed echoes, but rather the derivatives of such curves [4], called *sine* echoes. The extension of Solomon echoes to soft pulse excitation was later performed by Man [5, 6]. Butterworth [7] observed the superposition of an echo at $t = 2t_1$ arising from magnetic interaction upon inhomogeneity of the external field with the quadrupole echo. The advantage of different phases of $\pi/2$ pulses for first-order quadrupole echoes was demonstrated for ^{79}Br and ^{81}Br in alkali crystals [8], for ^{131}Xe in solid Xe [9] and for spin-5/2 nuclei [10]. Abe *et al.* [11] calculated analytically the oscillations of the echo amplitude for spin $I = 3/2$ and the case that the quadrupole interaction is either smaller or larger than the interaction with the RF pulses. The intermediate case was numerically investigated by Sobral *et al.* [12]. Mehring and Kanert [13] discussed the echo amplitude as a function of the angle of the second of two in-phase pulses and analyzed the lineshape of the spin echo for $I = 3/2$ through $I = 9/2$. Both quadrupole and magnetic broadening were taken into account for the echoes observed in vanadium compounds by Schoep *et al.* [14]. Mansfield *et al.* [15] were the first to analyze a three-pulse sequence and did so to study the cross-relaxation effects of $I = 3/2$ nuclei by. A comprehensive treatment of all three-pulse sequences was performed by Halstead *et al.* [16] using the multipole approach of Sanctuary [17, 18] for spin-3/2 nuclei subjected to *hard* RF pulses and an inhomogeneous distribution of quadrupole interactions and a local dipolar field. The multipole concept was also used in order to explain distinct relaxation times for the higher-rank polarizations in single crystals of KI (^{127}I, spin 5/2) [19]. Density matrix solutions for sequences of two *soft* pulses on $I = 3/2$ with $\eta = 0$ were given by Campolieti *et al.* [20]. Studies of a spin-3/2 system by an echo sequence without limitation to *hard* or *soft* pulses were performed by Man, who extended the two-pulse FID technique (see Section 2.7) with varying lengths of the second pulse [21] to echo studies [22, 23] and to spin-5/2 nuclei [24] and spin-7/2 nuclei [25], as well. Echoes in magnetically ordered substances were investigated by several authors [26-28]. Furó and Halle [29, 30] developed the two-dimensional quadrupole echo method for nuclei in anisotropic liquids with small quadrupole splitting and included powder samples. Mansfield [31] considered the selective excitation of the central transition and examined the echo after a sequence of two identical pulses under the influence of a homonuclear dipole interaction. Later a spin-echo Fourier transform NMR technique was used by Kunwar *et al.* [32] to obtain undistorted shapes of quadrupole-broadened central lines. Ernst *et al.* [33] showed that the *two-dimensional homonuclear separation on interaction method* can be used to separate the homonuclear dipolar interaction (ω_1) and Dolinsek [34] extended it to the inhomogeneous quadrupole interaction. Studies [32, 34] and the treatments of Haase and Oldfield [35, 36] and Furó and Halle [37, 38] took into consideration that only the central transition is excited and that the second-order quadrupole broadening of the observed central line is on the same order of magnitude as the dipole broadening. The use of echoes for the editing of ^{27}Al MAS NMR spectra of zeolite catalysts was shown by Schmitt *et al.* [39]. Echo techniques in combination with coherence selection (multiple-quantum filter) reduce the overlap of signals of quadrupolar nuclei in anisotropic soft matter, as demonstrated by Furo and Halle [29, 37]. Progress in this field was presented by Eliav *et al.* [40-43]. The connection between all NMR interactions (except the homonuclear dipole interaction) and the optimum experimental conditions for avoiding spectral distortions were described by Dumazy *et al.* [44].

Pascal Man was the most active scientist in the echo field at the end of the century. He considered second-order quadrupole effects on Hahn echoes under MAS conditions together with previous work on this topic [45] and presented a review of various quadrupolar effects on echoes in his contribution [46] to the *Encyclopedia of Analytical Chemistry*. Useful information can be found on his internet page http://www.pascal-man.com/. Previous-generation reviews of spin echoes for half-integer quadrupolar nuclei were done by Freude and Haase [47] and by Chan [48].

The Carr-Purcell-Meiboom-Gill (CPMG) [49, 50] pulse sequence $\pi/2_x$, (t_1, π_y, t_1)n can be considered an advanced concept of the Hahn echo. A quadrupole version, QCPMG, was established by Larsen *et al.* [51, 52] and will be considered in the last subchapter of this section.

3.2 Hard and Nonselective Pulses without Dipole Interaction

Fig. 3.1 gives the basic definitions for any two-pulse experiment. $\mathcal{H}^{\text{size}}$ was introduced by Eq (2.01). For hard pulses, $\mathcal{H}_{\text{RF}}^{\text{size}} \gg \mathcal{H}_{\text{Q}}^{\text{size}}$, the influence of the quadrupole interaction and a small resonance offset $\Delta\omega$ can be omitted during pulsing. Then, the Hamiltonians in Fig. 3.1 can be expressed in the interaction representations,

$$\mathcal{H}_1 = \hbar\omega_{\text{RF}} \exp(-\text{i}\phi_1 I_z)\, I_y \exp(+\text{i}\phi_1 I_z), \tag{3.01}$$

$$\mathcal{H}_2 = \frac{\hbar\omega_{\text{Q}}'}{6}\left(3I_z^2 - I(I+1)\right) + \Delta\omega I_z, \tag{3.02}$$

$$\mathcal{H}_3 = \hbar\omega_{\text{RF}} \exp(-\text{i}\phi_2 I_z)\, I_y \exp(+\text{i}\phi_2 I_z); \tag{3.03}$$

see Eqs. (1.30) and (1.61).

By defining

$$k_x = \cos\phi_1 \sin(\omega_{\mathrm{RF}}\tau_1),\;\; k_y = \sin\phi_1 \sin(\omega_{\mathrm{RF}}\tau_1),\;\;\; k_z = \cos(\omega_{\mathrm{RF}}\tau_1), \tag{3.04}$$

we have the observed NMR signal at the time t_2 [35]

$$E(t_1, t_2) \;=\; \sum_{j=x,y,z} k_j \sum_{m,m',m''=-I}^{+I} 2\,W_m \exp\,(\mathrm{i}A)\;\exp(\mathrm{i}(m' - m'' + 1)\phi_2)\,D\;\langle m'|I_j|m''\rangle, \tag{3.05}$$

where the dependence on t_1 and t_2 is contained in

$$A = \frac{1}{2}\omega_{\mathrm{Q}}'[(2m+1)t_2 + (m''^2 - m'^2)t_1] + \Delta\omega[t_2 + (m'' - m')t_1], \tag{3.06}$$

and D is a function of the Wigner rotation matrices (see Table 1.1),

$$d^I_{m',m}(\beta) = \langle m'|{-\mathrm{i}\beta I_y}|m\rangle \tag{3.07}$$

with

$$D = \; d^I_{m,m'}(\omega_{\mathrm{RF}}\tau_2)\; d^I_{m'',m+1}(-\omega_{\mathrm{RF}}\tau_2). \tag{3.08}$$

For the first sum in Eq. (3.06), $j \;=\; z$ describes the action of the second pulse on I_z, which is simply the FID for a nonselective excitation and will not be considered further.

For hard and nonselective pulses, it follows from Eq. (3.05) that if $\Delta\omega \;= 0$, the influence of ω_{Q}' vanishes for

$$(2m+1)t_2 + (m''^2 - m'^2)t_1 = 0. \tag{3.09}$$

Several echoes at times $t_2 \;=\; k\,t_1$ are possible [3]. For $I = 3/2$ and $I = 5/2$ we find from Eq. (3.09) echoes for $k = 1/2, 1, 3/2$ and $k = 1/2, 1, 3/2, 2, 3$, respectively. Inspection of the Eq. (3.05) matrix elements $\langle m'\,|I_j|m''\rangle$ reveals that for $j = x, y$ the values for m', m'' are restricted to $|m'' - m'| \;=\; 1$. Therefore, the allowed echoes are $k = 1$ for $I = 3/2$; $k = 1/2, 1, 2$ for $I = 5/2$.

From Eq. (3.06) it follows that, as long as $\Delta\omega$ is the same for all nuclei of the powder, each Solomon echo shows a phase factor. However, an anisotropy of the chemical shift or an inhomogeneous dipole interaction makes $\Delta\omega \neq 0$, and the contributions of all nuclei will cancel each other out. From Eq. (3.06) we obtain

$$t_2 = \frac{\frac{1}{2}\,\omega_{\mathrm{Q}}'(m' + m'') + \Delta\omega}{\frac{1}{2}\omega_{\mathrm{Q}}'(2m+1) + \Delta\omega}(m' - m'')t_1, \tag{3.10}$$

and it can be seen that if $\Delta\omega$ is not the same for all nuclei, an echo forms when $(2m+1) \;=\; (m' + \,m'')$. Thus, only the echo at $t_2 \;=\; t_1$ remains. This is why oriented material must be investigated for studies of quadrupole echoes in the case $t_2 \;\neq\; t_1$.

The amplitude of the echoes can be calculated from Eq. (3.05) with the help of Wigner rotation matrices. As was shown by Bonera and Galimberti [8] and Warren and Norberg [9], the maximum echo is obtained for $\phi = \;90°$ and $\omega_{\mathrm{RF}}\tau_1 = \omega_{\mathrm{RF}}\tau_2 = \pi/2$.

Introducing $t = t_2 - kt_1$ into Eq. (3.05), the dependence of $E(t, t_1, t_2)$ on t yields the k-th echo due to the different transitions, and shows that the second half of the echo shape is equivalent to the free induction decay (FID).

3.3. Soft Pulses without Dipole Interaction

For soft pulses, $\mathcal{H}_{\mathrm{RF}}^{\mathrm{size}} \lesssim \mathcal{H}_{\mathrm{Q}}^{\mathrm{size}}$, $\mathcal{H}_{\mathrm{D}}^{\mathrm{size}}$, $\mathcal{H}_{\mathrm{CSA}}^{\mathrm{size}}$, the influence of the quadrupole interaction during the pulse has to be considered; see Sect. 2.4.

As a consequence of soft, partly selective excitation, the density operator after the first pulse is no longer proportional to I_x or I_y , and the selection rule $| m' - m''| = 1$, following from $\langle m' | I_j | m'' \rangle$ in Eq. (3.05), is no longer valid. In other words, the spectral energy density of excitation for a satellite transition with a large frequency offset may be very weak, so that in Eq. (3.03), $\langle m | I_y | m-1 \rangle \approx 0$. Thus, additional echoes derived from Eq. (3.09) may now be observed. These are called *forbidden echoes* [3, 4].

3.4 Dipole Interaction for First-Order Quadrupole Echoes

The heteronuclear dipole interaction, which is proportional to $I_z S_z$, can generally be removed by the application of a second π-pulse. However, a strong coupling amongst S-spins, as well as a short spin-lattice relaxation of S-spins, can destroy the formation of the I-spin echo.

If the homonuclear dipole interaction is large compared to the quadrupole interaction, $\mathcal{H}_{\mathrm{D}}^{\mathrm{size}} \gg \mathcal{H}_{\mathrm{Q}}^{\mathrm{size}}$, its influence is essentially the same as for spin-1/2 nuclei [31]. If the homonuclear dipole interaction is as strong as the quadrupole interaction, $\mathcal{H}_{\mathrm{D}}^{\mathrm{size}} \approx \mathcal{H}_{\mathrm{Q}}^{\mathrm{size}}$, the spin flipping may be restricted to equivalent nuclei and a single transition. The restriction depends on the orientation of the EFG tensor with respect to the static magnetic field. If the quadrupole interaction is large compared to the dipole interaction, $\mathcal{H}_{\mathrm{Q}}^{\mathrm{size}} \gg \mathcal{H}_{\mathrm{D}}^{\mathrm{size}}$, the spin exchange due to homonuclear dipole interaction between adjacent levels can be considered as being completely suppressed, and the echo decay can be investigated by selective, separate excitation of each transition.

3.5 Selective Excitation of a Single Transition without Dipole Interaction

If $\mathcal{H}_{\mathrm{Q}}^{\mathrm{size}} \gg \mathcal{H}_{\mathrm{RF}}^{\mathrm{size}} \gg \mathcal{H}_{\mathrm{D}}^{\mathrm{size}}$, one can safely tune to any transition for single crystals or mainly excite the central transition for powders. This can be described by the reduced spin-1/2 formalism [4].

As outlined in Section 2.3, by tuning to the appropriate transition and omitting operators proportional to the unity operator, one has merely to replace I_z, I_z^2, I_y as follows:

$$I_z \to aS_z, \qquad I_z^2 \to (2m+1)S_z, \;\; I_y \to 2W_m S_y. \tag{3.11}$$

For the intensity of a single transition and a pair of in-phase 90°–180° selective pulses, i.e. for which $2W_m\, \omega_{RF}\, \tau_1 = \pi/2$, $2W_m\, \omega_{RF}\, \tau_2 = \pi$, and $\phi_1 = \phi_2 = 0$, the analogue to Eq. (3.05) is [47]

$$E(t_1, t_2) = \langle S_- | \exp(-\mathrm{i}\Omega S_z t_2) \exp(+\mathrm{i}\Omega S_z t_1) | S_z \rangle, \tag{3.12}$$

where Ω represents some remaining resonance offset, e.g. due to second-order quadrupole interaction. An echo is observed at $t_2 = t_1$ in full analogy to spin-1/2 nuclei subjected to an inhomogeneous interaction.

3.6 Selective Excitation of the Central Transition with Dipole Interaction

The calculation of the decay of the spin-echo envelope in the presence of dipolar interactions and second-order quadrupole interactions is rather complicated. The decay can be discussed in terms of the second moment spin-echo envelope decay, following the work by Haase and Oldfield [36]. We focus here on the central transition. The original literature [36] also treats the satellite transitions, and uses the assumption that all nuclei are subjected to the same quadrupole coupling; this implies homonuclear dipolar interaction and the same magnitude and orientation of the electric field gradient.

The first-order quadrupolar interaction dominates, and the interaction of the spins with the RF field is assumed to exceed the second-order quadrupolar contributions as well as the dipolar interactions among the spins. One retains during pulsing the Hamiltonian $\mathcal{H}_{1,3}$ (see Fig. 3.1), with the first-order quadrupolar term and the first-order part of the RF excitation. In the absence of RF excitation, one considers for $\mathcal{H}_3$ the first-order and second-order quadrupole effects and the first-order dipolar interaction.

In order to determine the spin-echo decay behavior, the second moment, $M_{2\mathrm{E}}$, of the envelope of a train of echoes is calculated as

$$M_{2\mathrm{E}} = -\frac{\mathrm{d}^2}{\mathrm{d}(2t_1)^2} E(2t_1)\bigg|_{2t_1=0} \tag{3.13}$$

In Ref. [36] it is shown that $M_{2\mathrm{E}}$ can be expressed by

$$M_{2\mathrm{E}} = E\,\frac{\mu_0}{4\pi}\,\gamma^4\,\hbar^2 \sum_j b_{i,j}^2 \qquad \text{and} \qquad M_{2\mathrm{E}} = F\,\frac{\mu_0}{4\pi}\,\gamma^4\,\hbar^2 \sum_j b_{i,j}^2, \tag{3.14}$$

where E and F describe spin-dependent factors with and without quadrupole interaction, respectively. The equation

$$b_{i,j} = \frac{3}{2}\,\frac{1-3\cos^2\beta_{i,j}}{r_{i,j}^3} \tag{3.15}$$

denotes the dipolar function (before powder average) of the inter-nuclear distance, $r_{i,j}$, and the inter-nuclear angle, $\beta_{i,j}$, with respect to the external magnetic field; see Section 1.5.

Second moments for like spins (homonuclear dipolar interaction) without quadrupole interaction are discussed in Section 1.5. Haase and Oldfield [36] calculated the ratios E/F (see Eqs. (3.14)) for $I = 3/2,\ 5/2,\ 7/2,\ 9/2$ and found a deviation from the factor of $4/9$ of less than 4%. The factor $4/9$ is expected, since like spins under the influence of strong quadrupole interaction behave like unlike spins. Spin-flipping is then prohibited between different transitions. This means that then the I-spins are hypothetically unlike spins which can be described by one gyromagnetic ratio, γ_{I}.

3.7 Second-order Quadrupole Effects on Hahn Echoes Under MAS Conditions

MAS frequencies of about 30 kHz are widely used now for the observation of NMR spectra of quadrupolar nuclei. The acquisition of the Hahn echo decay with a pulse distance of one rotation period eliminates the loss of signal during the ring-down of the probe and the recovery of the receiver immediately after the pulse, if the pulse duration is short compared to the rotation period and the static second-order quadrupole broadening and the static dipolar broadening of the signal are small compared to the MAS frequency. These conditions are fulfilled for the majority of applications; therefore, fast MAS in connection with a Hahn echo (selective pulse sequence $\pi/2_{\alpha}$, τ_{rot}, π_{β}, τ_{rot}, acq$_{\gamma}$) and a 16-step phase cycle for α, β and γ [32] are often applied in solid-state NMR spectroscopy of quadrupolar nuclei.

Man [45] considered second-order quadrupole effects on echoes under MAS conditions in detail. By analyzing single- and multiple-quantum transition echoes at different times he found that only the single-quantum Hahn echo that appears in our notation (see Fig. 3.1) at time $t_2 = t_1$ provides quantitative results on the spin population. An extended report about echoes can be found in his review article [46].

3.8 Intensity Measurements for Very Strong Quadrupole Coupling

The relaxation function $G^{\mathrm{sel}}_{-1/2,1/2}(t \lesssim 10\ \mu\mathrm{s})$ cannot be exactly measured immediately after a single preparation pulse at $t = 0$, because of the loss of signal during the ring-down of the probe and the recovery of the receiver immediately after the pulse. We use $\Delta\nu = 1/\,(\pi T_2)$ as a rough relation between the spectrum width $\Delta\nu$ and the decay time of the FID, T_2. Then we find that an intensity measurement by single-pulse excitation is not possible for a spectrum width of about 100 kHz or more. The width of the central transition spectrum has for $\eta = 1$ the maximum value $(\nu_{\mathrm{Q}}^2/3\nu_{\mathrm{L}})[I(I+1) - 3/4]$; see Fig. 1.3. For the quadrupole parameter ν_{Q} , it follows that we should meet the condition $(\nu_{\mathrm{Q}}^2/\nu_{\mathrm{L}})(\pi/3)[I(I+1) - 3/4] \ll 1/10\ \mu\mathrm{s}$ for intensity measurements by single pulses. This is not possible for overly strong quadrupole coupling. This problem can be overcome by the application of a Hahn echo with a pulse delay which slightly exceeds the time required for the ring-down of the probe and recovery of the receiver. The RF power should be adjusted for the selective excitation of the central transition.

3.9 Application of the Carr-Purcell-Meiboom-Gill Pulse Sequence

The Carr-Purcell-Meiboom-Gill (CPMG) [49, 50] pulse sequence, $\pi/2_x$, $(t_1,\ \pi_y,\ t_1)\,n$ was introduced in the first decade of the NMR history as an advanced concept of the Hahn echo. Diffusion effects in liquids have been shown to influence the behavior of the Hahn-echo decay as a function of the pulse distances, if the envelope of the echoes is measured as a function of the pulse distance. The diffusion in liquids has a lower influence on the decay of the echoes in the case of a fixed pulse distance. For the full-echo observation, the distance between $\pi/2$- and π-pulses should be set to the time necessary for the full decay of the free induction. This means that the distance between the π-pulses corresponds to the time τ_{a} required for the observation of a full echo; see Fig. 3.2. At present, we find very few applications of the CPMG pulse sequence for the monitoring of the echo envelope decay as a function of the pulse distances. The main focus of the CPMG applications is now the enhancement of the signal-to-noise ratio. If we neglect the decaying amplitude of the echoes, a full Hahn-echo observation increases the signal-to-noise ratio with respect to the measurement of the free induction decay, by a factor of $\sqrt{2}$. And by the acquisition of 100 echoes of a CPMG signal the signal-to-noise ratio increases by a factor of $\sqrt{100} = 10$ with respect to the observation of one full echo. However, the decay of the echo envelope can reduce these factors to zero. The echo envelope is described by a transverse relaxation time T_2^{echo} without rotation or $T_2^{\mathrm{MAS\ echo}}$ with MAS. The homonuclear dipolar interaction contributes predominantly to the corresponding relaxation process. The echo envelope is then described by the function

$$f_{\mathrm{envelope}}^{\mathrm{echo}} = \exp\left(-\frac{n\,\tau_{\mathrm{a}}}{T_2^{\mathrm{echo}}}\right) \quad \mathrm{or} \quad f_{\mathrm{envelope}}^{\mathrm{MAS\ echo}} = \exp\left(-\frac{n\,\tau_{\mathrm{a}}}{T_2^{\mathrm{MAS\ echo}}}\right), \tag{3.16}$$

where τ_a is the duration of a full echo (see Fig. 3.2) and n denotes the order of the echo. The full-echo observation of a simple Hahn echo corresponds to $n = 1$. For a very short transverse relaxation time with $T_2^{\mathrm{echo}} = \tau_a$, the amplitude of the first echo (with respect to the maximum free induction) is reduced by $\exp(-1)$, the second by $\exp(-2)$, and so on. This means that the application of a CPMG group makes no sense for relatively short transverse relaxation times.

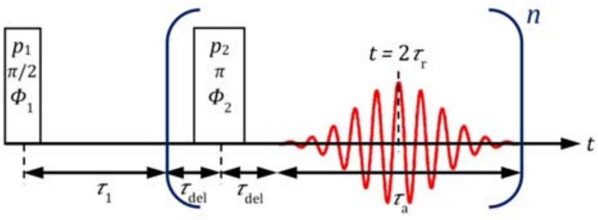

Fig. 3.2. Sketch of the CPMG pulse experiment. p_1 and p_2 represent the durations of the π/2- and π-pulses, respectively. The phases Φ_1 and Φ_2 have a difference of 90°. The acquisition interval of a full echo is denoted by τ_a. The delay time, τ_{del} , accounts for ring-down effects. The CPMG pulse sequence consists of one π/2-pulse for excitation and n successive π-pulses for refocusing. This means that n full echoes are monitored. The condition $2\,\tau_r = 2(\tau_1 + \tau_{del}) = \tau_a + 2\,\tau_{del}$ holds, and the pulse durations must be considered for the pulse spacing. τ_r should be the reciprocal rotation frequency or an integer multiple of it, if MAS is applied.

Figure 3.2 shows a sketch of the CPMG pulse experiment. The Fourier transform of a full echo in the time domain to an absorptively-phased spectrum in the frequency domain requires a first-order phase correction of about $360° \times \tau_a /2 \times 1/\tau_{\mathrm{sample}}$, where τ_a is the acquisition interval (or acquisition time) of the full echo; see Fig. 3.2. τ_{sample} denotes the sampling interval, which means the time difference between two adjacent complex data points in the acquisition time domain. Respectively, we have $1/\tau_{\mathrm{sample}}$ as the sampling bandwidth (or spectral width or sweep range) in the frequency domain after the Fourier transform. The term "dwell time", dw, is used in some cases as dw = τ_{sample} or the acquisition interval, but it has also been used as dw = τ_{sample} /2 (Bruker convention), since real and imaginary data points were sequentially sampled in the past.

Larsen *et al.* introduced for quadrupolar nuclei a quadrupole version of CPMG without MAS [51] and with MAS [52]. This so-called QCPGM was also introduced for ^{2}H NMR [53] and for MQMAS NMR [54]. Molecular dynamics of half-integer quadrupolar nuclei [55] was studied by QCPMG as well.

QCPMG was introduced with a 16-step phase cycle [51]. But Hung and Gan [56] have shown that a simple 2-step phase cycle with a phase shift of 90° between the exciting π/2-pulse and all following π-pulses gives maximum sensitivity and minimum distortions of the signal. This means that QCPMG returned to the original notion of CPMG with specified phase differences between pulses, as introduced by Meiboom and Gill [50]. The pulse sequence allows an intensity enhancement up to one order of magnitude for selected spectra, and a factor of about 3 is obtained in many cases. The Web of Science refers to 74 QCPMG studies in the years 1998–2012, among them 52 MAS studies. Hung and Gan [56], Schurko [57] and Polenova *et al.* [58] reviewed some of these studies.

As described above the echo envelope decay depends on the homogeneous dipolar interaction of the spins. We measured the ^{27}Al MAS NMR spectrum of andalusite (Al_2SiO_5) at ν_L = 195 MHz and ν_{rot} = 30 kHz [59]. The value $\tau_a/2$ = 3 ms was adjusted by the evaluation of the FID. But a strong transverse relaxation caused that the echo intensity after π/2- τ_a/2-π-τ_a/2 reached only 6% of the intensity of the maximum free induction. An exponential fit of the echo envelope for different values of the pulse distance yields $T_2^{\mathrm{MAS\ echo}} = 1.5$ ms. This is an example of how CPMG cannot enhance the sensitivity in the case of strong homonuclear dipolar interaction and short transverse relaxation time.

3.10 References

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