In the following sections, we want to elucidate the meaning of multiple quantum (MQ) coherence in the special case of dipolar coupled spin-$\frac{1}{2}$ systems, and to illustrate how the experiment is accomplished to produce and detect such a phenomenon. We will focus our interest to the excitation and detection of MQ and double quantum (DQ) coherence on the proton ($^1$H) systems under static and MAS experimental conditions, respectively.

The first experimental evidence of MQ phenomenon was made by the CW NMR spectroscopy in the end of 1950s. But until the mid 1970s the time domain MQ spectra of this kind were not investigated, because the theoretical and experimental methods of average Hamiltonian theory were not sufficiently developed. The literature overview of most of the important methods and applications of this phenomenon through 1980 can be found in [Bod81]. A highly detailed analysis of the major theoretical concepts and experimental techniques up to the middle of 1982 was made in [Wei83]. The first solid state MQ experiments were done in the group of A. Pines ([Mun87, Wei83]) in the middle of 1980s. They have used the samples (like Benzene partially oriented in nematic liquid crystal) where no other NMR methods were necessary to improve the spectral resolution, because the dipole-dipole coupling between spins was much reduced due to the high mobility of the system. In this chapter it will be also shown how MQ methods can be combined with the MAS experiment to get the high resolution spectra in solids.
2.1 Basics definitions

The definition of the coherence is based on the expansion of the time-dependent wave function $|\Psi(t)\rangle$ of the system in terms of stationary basis function $|i\rangle$:

$$|\Psi(t)\rangle = \sum_{i=1}^{n} c_i(t) |i\rangle \quad (2.1)$$

with time dependent coefficients $c_i(t)$ and $n$ as the dimension of the Hilbert space. A coherence between states $|r\rangle$ and $|s\rangle$ exist when the ensemble average of the product of coefficients

$$\rho_{rs}(t) = c_r(t) c_s^*(t) \quad (2.2)$$

does not vanish ([Sli92]). The elements $\rho_{rs}(t)$ defined by equation (2.2) forms the density matrix. It has to be noted that a coherent state is not an eigenstate of the Hamiltonian operator and it is time dependent. The coherent state should not by exchange with the statistical ensemble where the spins can be always found in the eigenstates $|r\rangle$ and $|s\rangle$.

In the high field NMR the Zeeman interaction cause the splitting of the energy levels according to the field direction and the difference between magnetic quantum numbers

$$\Delta m_{rs} = m_r - m_s \quad (2.3)$$

defines the order of coherence. In general, a matrix element $\rho_{rs}$ represents $p$-quantum coherence ($p = m_r - m_s$).

One special case of the coherence is a single quantum (SQ) coherence ($\Delta m_{rs} = \pm 1$), which corresponds to an observable transverse magnetization. It can be excited e.g. by the one 90°-pulse like was shown in the section 1.5. Such a coherence corresponds to the NMR signal, which is induced in the detection coil and can be directly observed. It can be schematically represented by the transitions between two energy levels $|\uparrow\rangle$ and $|\downarrow\rangle$ for one isolated spin $I = \frac{1}{2}$, where $\uparrow$ reflects the "spin-up" state and $\downarrow$ the "spin-down" state of the spin.

Let us consider a spin pair, where are four Zeeman energy levels corresponding to the four possible states, which can be noted $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$. In the case of homonuclear spins (i.e. $\gamma_1 = \gamma_2$), the energy levels corresponding to $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ are degenerated and three Zeeman levels remain that are equally spaced (see Figure 2.1a). Thus, one single NMR line would result in the spectrum from the 'allowed'\(^1\) ($p = \pm 1$)

\(^1\)Directly detected in the magnetization with the r.f. coil.
SQ transitions. This would be the result only if no coupling between them is taken into account. If now the dipolar coupling between is present, the resulting energy levels are slightly shifted due to the Hamiltonian $\hat{H}_D$ (see equation (1.28)). This shift is such, that the two allowed SQ transitions now have different frequencies (see Figure 2.1b). Hence, a splitting of the line by $2\omega_D$ results (see Figure 2.1b) which depends on the dipolar coupling strength. Coherence between the states $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ (see Figure 2.1), so-called double quantum (DQ) coherence, and between $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$, so-called zero-quantum (ZQ) coherence, is ‘forbidden’, that is, it cannot be detected directly. When extending this consideration from the two-spin system to a multiple-spin system, we find a wealthy of such $p$-quantum $(p \neq \pm 1)$ ‘forbidden’ coherence. We are calling it multiple quantum (MQ) coherence. In liquids it is caused by indirect spin-spin coupling ($J$-coupling) and in solids by direct dipolar coupling (Quadrupolar coupling is not considered). $J$-coupling is in solids usually very small with comparison to the direct dipolar coupling, so it will be not considered latter in this work.

**Figure 2.1:** Energy levels of a two-spin system with equivalent spins. a) Zeeman energy levels for the states $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $|\uparrow\downarrow\rangle$, and $|\downarrow\uparrow\rangle$. The allowed single quantum (SQ) transitions and ‘forbidden’ zero-quantum (ZQ) and double quantum (DQ) transitions are indicated. b) Energy level diagram of the spin pair including the effect of the dipolar coupling. The eigenstates of the Hamiltonian are now superpositions of the states $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $|\uparrow\downarrow\rangle$, and $|\downarrow\uparrow\rangle$, so-called triplet (symmetric) and singlet (antisymmetric) states. The energy levels of the triplet states $|1,1\rangle = |\uparrow\uparrow\rangle$, $|1,-1\rangle = |\downarrow\downarrow\rangle$ and $|1,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ are shifted compared to the Zeeman levels as indicated. Transitions between antisymmetric $|0,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ and symmetric states (triplet states) are not allowed. As indicated only SQ transitions are directly observable, so that the lines appear at the positions $\pm \omega_D = \frac{3}{2}d_{12}^2(3\cos^2 \vartheta - 1)$ in the spectrum. $d_{12}^2$ is the dipolar-coupling constant for two homonuclear spins (see the page 10).


2.2 Three pulse Experiment

A simple three pulse sequence [Aue76] was historically the first example of nonselective pulsed MQ excitation. It is capable to create coherences of orders zero through $N$ in a system of $N$ coupled spins-$1/2$. To understand the working of this basic experiment, we will once again consider a pair of dipolar coupled spin-$1/2$ nuclei. For convenience we will define initial state of the two spin system $I^i$ and $I^j$ through overall spin operator $\hat{I}_z$:

$$\hat{I}_z = \hat{I}_z^i + \hat{I}_z^j.$$  \hfill (2.4)

After the first $\frac{\pi}{2}$-pulse applied in the $x$-direction of the rotating frame the density matrix is found as a transverse magnetization (see section 1.5):

$$\dot{\rho}(0^+) = c\left(\hat{I}_y^i + \hat{I}_y^j\right) = c\hat{I}_y.$$  \hfill (2.5)

Just after the pulse the system evolves under the influence of dipolar Hamiltonian and for two coupled spins the Liouville-von Neumann equation (1.2) can be formally solved (see e.g. equation (1.79)):

$$\dot{\rho}(\tau^-) = c\hat{I}_y \cos \left[\omega^{ij}_D \tau\right] - 2c \left(\hat{T}^{ij}_{2,1} - \hat{T}^{ij}_{2,-1}\right) \sin \left[\omega^{ij}_D \tau\right]$$

$$\omega^{ij}_D = \sqrt{\frac{3}{8}} \alpha_{ij}^{IL} R_{2,0}^{ij}.$$  \hfill (2.6)

To excite DQ coherence the second pulse has to be applied. The best time $\tau$ for introducing that pulse is, when the second coefficient in equation (2.6) has the maximal value. This is the point when $\cos \left[\omega^{ij}_D \tau\right]$ (the first term) is zero. The schematic evolution of the $\hat{I}_y$ spin operator is shown in Figure 2.2. The result of the second pulse consist of two components:

$$\dot{\rho}(\tau^+) = c^{\pm \frac{\pi}{2}} \hat{I}_y \dot{\rho}(\tau^-) e^{-i \frac{\pi}{2} \hat{I}_x} = -c \hat{I}_z \cos \left[\omega^{ij}_D \tau\right] - i 2c \left(\hat{T}^{ij}_{2,2} - \hat{T}^{ij}_{2,-2}\right) \sin \left[\omega^{ij}_D \tau\right].$$  \hfill (2.7)

-----

$^2$Marks $\tau^{-/+}$ means before/after the r.f. pulse.

---

Figure 2.2: Optimal time $\tau$ for the second pulse in the three pulse experiment.
2. Multiple Quantum NMR

Figure 2.3: Excitation of double quantum coherence.

The first one represents to the longitudinal magnetization $\hat{I}_z$ and the second one describes the DQ coherence $\hat{T}_{2,\pm 2}$. According to the definition of $\hat{T}_{2,\pm 2}$ (see Appendix A) DQ coherence can be formally illustrated as the change of the orientation of the two spins at the same time (Figure 2.1):

$$\hat{T}^{ij}_{2,2} - \hat{T}^{ij}_{2,-2} = \frac{1}{2} \left( \hat{I}^i_+ \hat{I}^j_+ - \hat{I}^i_- \hat{I}^j_- \right).$$  \hspace{1cm} (2.8)

If the second pulse is applied at time $\tau = 1/\omega^D_{ij}$ (Figure 2.3) the first term in equation (2.7) vanishes and the DQ coherence will become maximal:

$$\hat{\rho}(\tau^+) = -i c \left( \hat{I}^i_+ \hat{I}^j_+ - \hat{I}^i_- \hat{I}^j_- \right).$$  \hspace{1cm} (2.9)

It is necessary to note that the coherence described by this equation is not visible in the magnetization because the expectation value vanishes ($\alpha = x, y$):

$$\text{Tr} \left\{ \hat{I}^{ij}_\alpha \hat{T}^{ij}_{2,\pm 2} \right\} = \text{Tr} \left\{ \hat{I}^{\alpha j}_i \hat{T}^{ij}_{2,\pm 2} \right\} = 0.$$  \hspace{1cm} (2.10)

To detect it the third last pulse called detection pulse has to be added after time $t_1$.

If we again assume the dipolar coupled spin pair, after the second pulse the DQ coherence does not evolve because the Hamiltonian operator $\hat{H}_D$ of the two dipolar coupled spin pair commute with the operator $\hat{T}^{ij}_{2,\pm 2}$:

$$[\hat{T}^{ij}_{2,0}, \hat{T}^{ij}_{2,\pm 2}] = 0.$$  \hspace{1cm} (2.11)

In this case the density matrix at time $t_1$ is given like

$$\hat{\rho}(\tau + t_1) = -c e^{-i\hat{H}_D t_1 \hat{I}_z} e^{i\hat{H}_D t_1} \left[ \omega^D_{ij} \tau \right] - i 2c \left( \hat{T}^{ij}_{2,2} - \hat{T}^{ij}_{2,-2} \right) \sin \left[ \omega^D_{ij} \tau \right].$$  \hspace{1cm} (2.12)

The first term also does not evolve under the dipolar Hamiltonian but it appears as detectable magnetization. But by means of the cycling of the phases of the pulses it can
be filtered out and we will not assume it in the next calculations. The second term in equation (2.12) describes DQ coherence which does not evolve during time $t_1$ (only when in resonance excitation is assumed, more details see section 2.4.2). The third $\pi$-pulse converts it to the SQ coherence and under the above spoken condition for excitation time $\tau = 1/\omega_D^ij$ the density matrix can be written as

$$\hat{\rho}(\tau + t_1^+) = e^{i\frac{\tau}{2}I_x} \hat{\rho}(\tau + t_1^-) e^{-i\frac{\tau}{2}I_x} = 2c \left( \hat{T}_{2,1}^{ij} - \hat{T}_{2,-1}^{ij} \right). \quad (2.13)$$

The terms $\hat{T}_{2,\pm1}^{ij}$ are still not visible in the magnetization but under the evolution due to dipolar coupling they can be detected and then

$$\hat{\rho}(\tau + t_1 + \tau') = 2c \left( \hat{T}_{2,1}^{ij} - \hat{T}_{2,-1}^{ij} \right) \cos \left[ \omega_D^ij \tau' \right] + c \hat{I}_y \sin \left[ \omega_D^ij \tau' \right]. \quad (2.14)$$

The second term in equation (2.14) represents the measurable magnetization induced in the detecting coil. It can be seen that the signal is maximal only when $\tau' = \tau$ (see Figure 2.4). To detect the DQ time-evolution it is not necessary to acquire whole spectrum but only one point at time $t_2 = 0$ (see Figure 2.4) is enough. The signal at this point is then given by

$$\hat{\rho}(\tau, \tau', t_1, t_2 = 0) = c \left( \hat{I}_y^+ + \hat{I}_y^- \right) \sin \left[ \omega_D^ij \tau \right] \sin \left[ \omega_D^ij \tau' \right]. \quad (2.15)$$

Under the optimal conditions for times $\tau$ and $\tau'$ the whole magnetization in the case of two spins interaction is transferred to the DQ coherence and at the end it is completely reconverted back. The signal is for the isolated spin-pair independent to evolution time $t_1$. An interesting information is not the modulation of the signal but the amplitude. It carries an information about the amount of the magnetization transferred to the DQ coherence at defined time $\tau$. If a system consists of more strongly coupled spin pairs their intensities in the spectrum carry the relative information about their strength. If in addition one of
the coupling strength is known the others can be calculated from their intensities. This
method will be more extensively used in this work.

If we assume now also chemical shift interactions, some additional terms have to be
added to the above calculations. More detailed description can be found in [Sli92] or
[Mun87]. It can be seen from their calculations that introducing chemical shifts and
resonant offsets the simple three pulse sequence (Figure 2.4) generates also SQ transverse
magnetization terms and other unwanted terms which can not be filtered out by the phase
cycling of the pulses. The problem can be overcome by inserting of a \( \pi \)-pulse midway into
the excitation period between the first and the second \( \frac{\pi}{2} \)-pulse. The resulting sequence
will after that look like

\[
\begin{align*}
\text{Excitation} & \quad (\frac{\pi}{2})_x \cdots \frac{\pi}{2} \cdots (\pi)_x \cdots \frac{\pi}{2} \cdots (\frac{\pi}{2})_x \cdots t_1 \cdots \\
\text{Evolution} & \\
\text{Reconversion} & \quad (\frac{\pi}{2})_{x,y} \cdots \cdots t_2 \cdots \\
\text{Detection} & 
\end{align*}
\]

It can be seen that in such a sequence chemical shift and resonant offset terms have
influence to DQ coherence only during evolution time \( t_1 \). The DQ coherence operator will
oscillate during time \( t_1 \) at the frequency defined by a sum of chemical shift frequencies for
two spins.

To study the time evolution of the multiple quantum (MQ) coherence the two-
dimensional experiment has to be accomplished where time \( t_1 \) is increased step by step.
At the certain point \( t_1 \) the time evolution of MQ coherence will be interrupted and trans-
ferred by the reconversion pulse to the transverse magnetization. Only the first point of
the time signal at \( t_2 = 0 \) is necessary to acquire to get the overall information. More
detailed description can be found in the next sections.

2.3 General scheme of MQ experiment

Any experimental attempt to monitor the dynamic evolution of the spin system in which
there exists a condition of multiple quantum (MQ) coherence must inevitably be used
upon the detection of single quantum (SQ) transverse magnetization. However, complex
the structure of a multilevel system may be, these relatively few magnetic dipole modes
still remain the only coherences directly observable with conventional radio-frequency (r.f.)
technology. Operating within this constraint, MQ experiments typically employ a method
of indirect detection using two-dimensional spectroscopy (see section 1.7) and then to
record their response to either naturally occurring or externally manipulated local fields.
The basics scheme for detecting MQ coherence is illustrated in Figure 2.5. The first part called *excitation* period is designed to excite MQ coherence by the proper design of the high frequency pulses. Selection of the correct pulse sequence is strongly dependent on the system which we want to study. The basic sequence was shown in the section 2.2. In the second part *evolution* period, MQ coherence evolves during time $t_1$ under the influence of local fields of the system and the strong static external field $\vec{B}_0$. Because MQ coherences can not be observed directly they have to be transferred to the SQ modes in the *reconversion* period. After this step they are still laying parallel to the $\vec{B}_0$ field and they can not be seen in the magnetization. To make them visible a last detection pulse has to be added to the sequence after which they can be acquired during time $t_2$ in the *detection* period by the conventional spectrometer. Only one condition has to be fulfilled for a reconversion operator $\hat{U}_{rec}$. It has to be equal to the time reversal excitation propagator $\hat{U}_{exc}^+$ ([Mun87]).

### 2.3.1 Excitation and Reconversion

In this part we will discuss the basic properties of the reconversion period and how it can be constructed from the excitation period. We will see that it depends on the order of coherence $p$ excited by the excitation Hamiltonian. Two Hamiltonian operators $\hat{H}_{exc}$ and $\hat{H}_{rec}$ will be used for description of the pulse sequence during excitation and reconversion period. To realize time reversal ([Yen83]) during the reconversion period the following condition has to be fulfilled:

$$\hat{U}_{rec} = \hat{U}^+_{exc} = \hat{U}^{-1}_{exc} = e^{i \hat{H}_{exc} t} \Rightarrow \hat{H}_{rec} = -\hat{H}_{exc}.$$ (2.16)

This leads to the simple modification of the excitation pulse sequence during reconversion period, which can be done by the phase shift. Let us define an angle of the phase shift as $\phi$ with the phase propagator $\exp(-i \phi \hat{I}_z)$. The reconversion Hamiltonian in this case can be written as

$$\hat{H}_{rec} = e^{-i \phi \hat{I}_z} \hat{H}_{exc} e^{i \phi \hat{I}_z}.$$ (2.17)
Let us assume the excitation Hamiltonian defined by the irreducible spherical tensors ([Meh83, Sli92]) \( \hat{H}_{\text{exc}} \approx A_{m,n} \hat{T}_{m,n} \), where \( A_{m,n} \) contains all lattice variables, which are under the phase rotation of the pulse sequence invariant. In this notation the quantum number \( n = -m, -m + 1, \ldots, +m \) can be identified with the coherence order \( p \) and the rank of the tensors \( m = 0, 1, \ldots, 2L \) defined through total spin quantum number \( L \), which represent the sum of the spin quantum numbers of the component nuclei (e.g. for two spins \( I = \frac{1}{2}, L = 1 \)). If we use the transformation property for the spin operators \( \hat{T}_{m,n} \) by \( e^{-i \phi \hat{I}_z} \hat{T}_{m,n} e^{i \phi \hat{I}_z} = e^{-i m \phi} \hat{T}_{m,n} \) (see [Ern87] p. 269 or [SR94] p. 108), we can express equation (2.17) as

\[
e^{-i \phi \hat{I}_z} (A_{m,n} \hat{T}_{m,n}) e^{i \phi \hat{I}_z} = e^{-i m \phi} A_{m,n} \hat{T}_{m,n}.
\] (2.18)

To fulfill the condition of the time reversibility of the reconversion Hamiltonian (see equation (2.16)), the condition for the phase shift \( \phi \) can be directly seen from the above equation:

\[
e^{-i m \phi} = -1 \quad \text{if} \quad \phi = \frac{\pi}{|n|}.
\] (2.19)

To find a correct reconversion sequence for any excitation sequence is than very simple. For \( n \)-quantum coherence all phases of the r.f. pulses have to be shifted by an angle \( \frac{\pi}{n} \). In this manner one has to find for an experiment only the correct excitation sequence.

### 2.4 Static MQ experiment

In this section MQ r.f. pulse sequences for static solids will be described. We will concentrate to the excitation and detection of high-order MQ coherences in proton (\(^1\)H) systems. Coherences of very high order are usually possible where an extensive network of dipolar couplings exist. Typical example are strongly coupled abundant nuclear spin-\(^1\)H systems like e.g. adamantane or hexamethylbenzene (HMB). In this systems the influence of a coupling between two spins on the development of the system depends on the time elapsed, with the value \( d_{ij}^{(1)} \tau \) (see equation (1.27) and Figure 2.5) providing a measure of the effectiveness of a particular pair interaction at each instant. When excitation time \( \tau \) is not enough long i.e. \( d_{ij}^{(1)} \tau \ll 1 \), the interaction between \( i \) and \( j \) spins is negligible. However, with increasing time \( \tau \) more couplings become sufficiently large to contribute to the resulting spectrum. In addition, the strongly coupled spins, which determine the early time

\(^3\)In this work 90°phase shift for \( n = 2 \) will be used as will be shown later.
development continue to influence the dynamics at later times. The growth of the so-called 'spin clusters' under the influence of a many body bilinear Hamiltonian is schematically shown in Figure 2.6. In general, for many number of coupled spins up to the effective 'size' of the system at time $\tau$, can be excited. In the next part we will introduce some pulse sequences which can monitor the evolution of the spin clusters.

2.4.1 Time reversal pulse sequences

Already over 16 years ago, Yen and Pines ([Yen83]) demonstrated the possibility to detect MQ coherences in strongly coupled systems of spins-$\frac{1}{2}$ in solids. Up to now there are plenty of time reversal multiple-pulse sequences, which are able to do it (reader is referred to overview monographs [Bod81, Wei83, Mun87]. The methods are developed further as a tool for estimating the sizes of nuclear spin clusters in solids ([Bau85, Shy88]). General scheme for such experiments is shown in Figure 2.5.

To understand the effect of these sometimes complicated pulse sequences one has to solve the density operator equation (1.3) under the action of various pulses and evolution Hamilton operators. This will lead in most of the cases to the cumbersome calculations, which can be avoided by considering of the evolution of the initial density operator in the presence of an average Hamiltonian. Such a treatment of Average Hamiltonian Theory (see section 1.3) requires the pulse sequence to be periodic (and cyclic) so that it is sufficient to calculate the average Hamiltonian for a limited number of pulses and evolution intervals,
Figure 2.7: A pulse sequence for double quantum excitation for static case. It can be repeated for increasing excitation time \( \tau \).

so-called cycle. We will make a small example for calculating the average Hamiltonian in the case of the pulse sequence shown in Figure 2.7 where the cycle consist of four \( x \)-pulses. It will be shown that this pulse sequence generates double quantum (DQ) average Hamiltonian in the first order approximation. Two methods of calculations will be presented. One a little bit more sophisticated requiring more calculations and the second one with the pictorial representation of the toggling frame Hamiltonian ([Ern87]).

We start with the evolution of the density operator under the action of the pulse sequence (Figure 2.7) with the cycle time \( 6\Delta \). We will assume \( \delta \)-pulses for simplicity. The density operator at the end of the cycle, for this pulse sequence, is given by

\[
\hat{\rho}(6\Delta) = \hat{U}(6\Delta) \hat{\rho}(0) \hat{U}^{-1}(6\Delta)
\]  
(2.20)

with the time-evolution operator ("propagator") for the full cycle\(^4\)

\[
\hat{U}(6\Delta) = \hat{L}^{(\frac{1}{2})}_z \hat{P}_x \hat{L}^{(2)}_z \hat{P}_x \hat{L}_z \hat{P}_x \hat{L}^{(2)}_z \hat{P}_x \hat{L}^{(\frac{1}{2})}_z ,
\]  
(2.21)

where \( \hat{P}_x = e^{i\gamma B_1 \hat{I}_x t_{rf}} \) is the pulse operator and \( \hat{L}^{(\frac{1}{2})}_z = e^{-i\hat{H}_z \frac{\Delta}{2}} \), \( \hat{L}_z = e^{-i\hat{H}_z \Delta} \) and \( \hat{L}^{(2)}_z = e^{-i\hat{H}_z 2\Delta} \) governs the evolution under the influence of the Hamiltonian \( \hat{H}_z \), which can be the Hamiltonian for homonuclear dipolar coupling \( \hat{H}_z = \hat{H}_{zz} = \hat{H}_{DD} \) (see equation (1.28)) or in the case of chemical shift \( \hat{H}_z = \omega_{CS} \hat{I}_z \) (see equation (1.22)). As initial density operator \( \hat{\rho}(0) \), we use \( \hat{\rho}(0) = c \hat{I}_z \) like in equation (1.38).

\(^4\)Interactions are going from right to left but because of the symmetry of this particular pulse sequence it has no importance.
Note, that all Hamiltonians are characterized by spin operators so that the transformation of the spin operators by the pulses directly determines the transformation properties for the propagator $\hat{L}_z \left( \hat{P}_x = \hat{P}_x^{-1} \right)$

$$\hat{P}_x \hat{L}_z \hat{P}_x = \hat{L}_y \quad \text{and} \quad \hat{P}_y \hat{L}_z \hat{P}_y = \hat{L}_y^-.$$ \hspace{1cm} (2.22)

The corresponding transformation properties can be found also for $\hat{L}_x$ and $\hat{L}_y$. The minus sign in the superscript of the evolution operator in the second term of equation (2.22) reminds us that the corresponding spin operators have been transformed from $\hat{I}_\alpha$ to $-\hat{I}_\alpha$ ($\alpha = x, y, z$; e.g.: $\hat{H}_{zz} = \hat{H}_{zz}^\alpha$). The only difference between $\hat{L}_z$ and $\hat{L}_y$ (or $\hat{H}_z$ and $\hat{H}_y$) is that the corresponding spin operators $\hat{I}_z$ have been transformed to $\hat{I}_y$. For homonuclear dipolar Hamiltonian we will use abbreviation

$$\hat{H}_{yy} = -\sum_{i<j} \frac{d_{ij}^I}{2} \left( 3 \cos^2 \theta_{ij} - 1 \right) \left( 3 \hat{I}_y^i \hat{I}_y^j - \hat{I}_y^i \cdot \hat{I}_y^j \right). \hspace{1cm} (2.23)$$

Inserting unity operator $\hat{1} = \hat{P}_x^{-1} \hat{P}_x$ into equation (2.21) after each $\hat{L}_z$ operator and performing the transformation according to equation (2.22) we obtain

$$\hat{U}(6\Delta) = \hat{L}_z^{(\frac{1}{2})} \hat{L}_y^{(2)} \hat{L}_x \hat{P}_x \hat{L}_y^2 \hat{L}_z^{(\frac{1}{2})} \hat{P}_x \hat{P}_x \hat{P}_x \hat{P}_x \hat{P}_x,$$ \hspace{1cm} (2.24)

where the pulse propagators have been shifted one step to the right. Repeating this procedure two more times results in

$$\hat{U}(6\Delta) = \hat{L}_z^{(\frac{1}{2})} \hat{L}_y^{(2)} \hat{L}_z^{-1} \hat{L}_y^{-1} \hat{L}_z^{(\frac{1}{2})} \hat{P}_x \hat{P}_x \hat{P}_x \hat{P}_x \hat{P}_x,$$ \hspace{1cm} (2.25)

where the evolution and pulse propagators have been separated. Realizing that the four ($\frac{1}{2} \Delta$) pulses corresponds to a $360^\circ$ rotation and thus can be omitted (more formally using that the pulse sequence is cyclic, i.e. $\hat{U}_{rf} = \pm 1$ for the pulse cycle, where $\hat{U}_{rf}$ is the propagator corresponding to all pulses), we are left with a propagator from which the pulses are removed. This can be interpreted such that we transform from the conventional rotating frame to a frame fixed to the pulses, so-called the toggling frame. We therefore view the evolution Hamiltonian from this frame, which accounts for the change from $\hat{L}_z$ to $\hat{L}_y^-$ in two of the evolution intervals.

To analyze equation (2.25) further, let us make an approximation for short times $\Delta$. Expanding the exponential operators $\hat{L}_z$ and $\hat{L}_y$, multiplying the resulting terms and

\[ \text{For } \hat{H}_{xx} \text{ spin operators } \hat{I}_i^x \hat{I}_j^x \text{ are replaced by } \hat{I}_i^y \hat{I}_j^y. \]
sorting them according to their order we are getting that

\[ U(6\Delta) = 1 - i \left( \hat{H}_z + \hat{H}_z^- + 2(\hat{H}_y + \hat{H}_y^-) \right) \Delta + \text{higher orders} \approx e^{-i \hat{H} 6\Delta}. \] (2.26)

Exact calculation of the above equation will lead to so-called the Magnus expansion (see equations (1.54 - 1.56)). The first order approximation corresponds to the linear terms and can be written as

\[ \hat{H}^{(0)} 6\Delta = \left( \hat{H}_z + \hat{H}_z^- + 2(\hat{H}_y + \hat{H}_y^-) \right) \Delta. \] (2.27)

This lowest order of approximation is sufficient only for very short \( \Delta \) values. We will not deal with higher-order terms explicitly and only note that they contain commutators between the Hamiltonians at different times. For two-spin system these commutators are zero and our zero order treatment is exact. Whereas for a multiple-spin Hamiltonian higher-orders have to be calculated to obtain a satisfactory description of the pulse sequence. However, the zero-order average Hamiltonian always has to be derived as a first step, even if an analysis of higher-order terms is performed. The higher-order correction terms will be in this work considered only in the form of symmetry rules for the pulse sequence.

For calculation of the zero order homonuclear dipolar Hamiltonian \( \hat{H}^{II}_D \) with its bilinear form so that \( \hat{H}_z = \hat{H}_z^- = \hat{H}_{zz} \), we will obtain from equation (2.27)

\[ \hat{H}^{(0)}_D = \frac{1}{3} \left( \hat{H}_{zz} + 2\hat{H}_{yy} \right) = \frac{1}{3} \left( \hat{H}_{yy} - \hat{H}_{xx} \right). \] (2.28)

For the last step, so-called the magic-zero condition

\[ \hat{H}_{xx} + \hat{H}_{yy} + \hat{H}_{zz} = 0 \] (2.29)

has been used, which can be easily verified. It can be shown that equation (2.28) corresponds to the products of the raising and lowering operators ([Bau85]) \( \left\{ \hat{I}_z^+ \hat{I}_y^+ + \hat{I}_y^- \hat{I}_z^- \right\} \) for two spins \( I^i \) and \( I^j \), which represent \( \pm \)DQ coherence in the case of the two spin interaction.

The zero order chemical shift average Hamiltonian over the full cycle can also be calculated from equation (2.27) as

\[ \hat{H}^{CS^{(0)}} = \frac{1}{6} \left( \hat{I}_z - \hat{I}_z + 2(\hat{I}_y - \hat{I}_y) \right) = 0. \] (2.30)

Thus this sequence removes chemical shift (or offset terms) in the first order approximation.
Now the effect of such a 'pure' DQ zero-order average Hamiltonian (equation (2.28)) for two spin system on the initial density operator has to be calculated. It follows from its calculation for dipolar coupled two spins $I^i$ and $I^j$ under the initial density operator $\hat{\rho}(0) = c(\hat{I}^i_z + \hat{I}^j_z)$ that

$$
\hat{\rho}(\tau_c) = c \left( \hat{I}^i_z + \hat{I}^j_z \right) \cos[D^{ij} \tau_c] + i c \left( \hat{I}^i_+ \hat{I}^j_+ - \hat{I}^i_- \hat{I}^j_- \right) \sin[D^{ij} \tau_c] \quad (2.31)
$$

The cycle time is $\tau_c = 6\Delta$ in the case of $\delta$-pulses. From equation (2.31) it can be directly seen that the second coefficient represents to DQ coherence and thus the pulse sequence shown in Figure 2.7 excite DQ transitions. The first part of the mentioned equation corresponds to the longitudinal magnetization and without additional cycling of the pulses it can not be removed out from the resulting spectrum. For more detailed discussion about equation (2.31) see section 2.2.

So far, we have concentrated on the zero-order analysis, which is not each time sufficient. For optimizing multiple-pulse sequences, however, it is useful to be aware of some few symmetric principles for elimination of higher-order terms. The so-called 'super' cycles that is, well designed combination of the different variants of the basic cycles can be used for this purpose. The design of such super-cycles is possible when the zero-order chemical shift (or offset terms) vanishes for a basic cycles. Then higher-order effects left over by the basics cycles are additive and thus when generated with the opposite sign in two following periods will cancel each other. Odd-order correction terms in the Magnus expansion, for instance, can be cancelled using super-cycles that are symmetric with respect to the toggling-frame states ([Hae76]). Four pulse sequence shown in Figure 2.7 fulfills the condition for the symmetric cycle for the toggling-frame states as will be shown in the next section.

Finite pulse lengths can also contribute to the resulting spectrum in the detection period and therefore it is useful to eliminate their effects. This can be done by designing the reflection symmetric pulse sequences. Our four pulse sequence than does not fulfill this condition and has to be extended as will be shown is section 2.4.1.2.

### 2.4.1.1 Determining toggling-frame states for four pulse sequence

For analysis of multiple-pulse sequences under the average Hamiltonian theory toggling frame states have to be calculated. Let us assume for the moment infinite narrow r.f. pulses,
represented by the transformation $\hat{P}_\alpha \hat{P}_\beta \cdots \hat{P}_\eta (\alpha = \pm x, \pm y)$ and separated by free precession periods. Each pulse rotates the toggling frame into a new position, where the toggling frame Hamiltonian $\hat{H}(t)$ (see equation (1.45)) remains constant. For the interval $\Delta_k$ between two pulses $k$ and $k+1$ it can be then written $\hat{H}(t) = \hat{H}(k)$ and the toggling Hamiltonian can be calculated by stepwise transformations

\[
\hat{H}(0) = \hat{H}_{\text{int}} \\
\hat{H}(1) = \hat{P}^{-1}_\alpha \hat{H}_{\text{int}} \hat{P}_\alpha \\
\hat{H}(2) = \hat{P}^{-1}_\alpha \hat{P}^{-1}_\beta \hat{H}_{\text{int}} \hat{P}_\beta \hat{P}_\alpha \\
\vdots
\]

where $\hat{H}_{\text{int}} = \hat{H}_z$ represents the secular Hamiltonian for particular interaction. It is important to note an unexpected order of the transformation in equation (2.32). All previous pulses are arranged in reverse order and appear with reversed sense of rotation ([Ern87]).

The zero-order average Hamiltonian is obtained from a weighted sum

\[
\hat{H}^{(0)} = \frac{1}{\tau_c} \sum_{k=0}^{n} \Delta_k \hat{P}^{-1}_\alpha \cdots \hat{P}^{-1}_\eta \hat{H}_{\text{int}} \hat{P}_\eta \cdots \hat{P}_\alpha.
\] (2.33)

This analysis enables us to make the detailed description of a pulse sequence. Determination of the toggling frame states are also the basics for calculating average Hamiltonians of the higher orders, which leads to the Magnus expansion series (see section 1.3). Usually multiple-pulse sequences are designed to remove higher order terms (or to suppress them to have negligible influence) and then only zero-order average Hamiltonian became of importance.

According to equation (2.32) the graphical representation of the toggling frame states can be done ([Haf98]). It is based on simple rotations of the spin operators. Rotations in the spin space can be performed quite easily, either by a suitable computer program, or by the help of a cube that is rotated. This graphical determination of the toggling frame states provide us much simple and intuitively more appealing model than sometimes cumbersome calculations presented in the previous section. A sketch of such a cube, which serves as a simple model for the toggling frame is shown in Figure 2.8. Each of its sides is labelled by the corresponding operator $\hat{I}_\alpha$, where $\alpha = \pm x, \pm y, \pm z$, so that a right-handed coordinate system is built. The cube is placed on a plane, where $x$ and $y$ axis are drawn indicating the orientation of the corresponding r.f. pulses. In the initial state this 'magic cube' is
2.4. Static MQ experiment

Figure 2.8: The 'magic cube', a convenient tool for determining toggling-frame states \( \hat{I}_x, \hat{I}_y, \hat{I}_z \) for the given pulse sequence. The cube is oriented so that the initial state \( \hat{I}_z \) is pointing upwards. The cube is rotated around the two fixed axes \( x \) or \( y \) according to the pulse sequence. The spin operator that is pointing upwards for each rotation step reflects the toggling-frame state for the corresponding time interval.

oriented such, that \( \hat{I}_z \) operator is up and the \( \hat{I}_x \) and \( \hat{I}_y \) operators are pointing in the direction of the corresponding axes as shown in the drawing. Now, the investigated pulse sequence can be analyzed pulse by pulse in the straightforward way by simple rotating the cube around the two fixed axes in accordance with the pulse sequence. In our case the rotations have left handed sense. It hangs on the definition of the \( \vec{B}_1(t) \) field (see equation (1.14)). The toggling-frame state for each rotational step is then determined by the operator, which is pointing upwards.

Using this simple cube model the four pulse sequence introduced in the previous section can be analyzed. Corresponding toggling frame states for the dipolar interaction and the chemical shift interaction are shown in Figure 2.9. After that, according to equation (2.33), zero-order average Hamiltonian can be directly calculated. It can be simply shown that average Hamiltonians for the particular interaction have the same form as in equations (2.28) and (2.30). Reflection symmetry of a cycle to the toggling frame states can be easily recognized from Figure 2.9.

It should be stressed, that such a simple 'magic cube' formalism for determining toggling frame states and follow-up zero-order average Hamiltonian can be used only in the case of \( \delta \)-pulses. For pulses of finite length equation (2.33) is not more valid and has to be extended by the duration of the pulses, where toggling frame changes continuously.
Figure 2.9: The four pulse sequence for DQ excitation with the given toggling frame states for chemical shift and dipolar interaction. The rotation of the coordinate system, known as toggling frame is schematically drawn.

It can be calculated that for our four pulse sequence the contribution of this parts to the average Hamiltonian is additive and thus lead even in the first order approximation to the incorrect results. This imperfections can be avoided by adding additional period of the pulses shifted by 180° as will be shown in the next section.

2.4.1.2 Eight pulse sequence

Most extensively used pulse sequence for exciting multiple quantum coherences in static solids was at the beginning of eighties in the group of A. Pines, eight pulse sequence. With its two versions adopted from J. Baum et al. ([Bau85]) it is shown in Figure 2.10. Both pulse sequences consist of eight $\frac{\pi}{2}$-pulses of duration $t_p$ separated by delays $\Delta$ and $\Delta' = 2\Delta + t_p$. On contrary to the previous section where $\delta$-pulses were assumed, period $\Delta'$ was enlarged by the duration of the $\frac{\pi}{2}$-pulse, $t_p$, for proper zero-order average Hamiltonian. These pulse sequences can excite even order coherences for homonuclear dipolar coupling and their zero-order even-quantum average Hamiltonian is derived as ([War80, Bau85])

$$\hat{H}_{D,8p}^{(0)} = - \sum_{i<j} D_{ij} \left( \hat{T}_{ij}^{+} + \hat{T}_{ij}^{-} \right)$$

(2.34)

$$D_{ij} = \frac{\mu_0h}{4\pi} \frac{\gamma^2}{r_{ij}^3} \frac{1}{2} \left( 3 \cos^2 \theta_{ij} - 1 \right).$$

Equation (2.34) represents for two spin system ‘pure’ DQ operator. The cycle time $\tau_c$ is equal to $12(t_p + \Delta)$ for both pulse sequences. Due to their reflection symmetry the part, where toggling frame changes continuously (during r.f. pulses), from the zero-order
2.4. Static MQ experiment

Figure 2.10: Two time reversal pulse sequences for exciting multiple quantum coherences for static solids. Excitation and reconversion time can be increased by repeating of the pulses \( N \) times. In the case of \( \delta \)-pulses \( \Delta' = 2\Delta \), but for finite pulse length \( t_p \) it has to be increased to \( \Delta' = 2\Delta + t_p \).

average Hamiltonian is removed and in addition also \( \hat{H}_{D,8p}^{(0)} = 0 \) (equation (1.55)). Pulse sequence shown in Figure 2.10a is preferred whenever resistance to resonance offset effects during excitation and reconversion is particularly important. On the other hand pulse sequence in Figure 2.10b is more appropriate in cases when r.f. field inhomogeneity is a serious problem. In this work experimental results were made with pulse sequence b). It can be seen (see section 2.4.1) that chemical shift interaction (or offset terms) are removed from the average Hamiltonian in the case when \( \| \hat{H}_D \| \gg \| \hat{H}_{CS} \| \), which is a limitation for using eight pulse sequence. To avoid relaxation of the multiple quantum signal during excitation and reconversion period the cycle time \( \tau_c \) has to be enough small, i.e. \( \| \hat{H}_D^{(0)} \| \tau_c \ll 1 \). Beyond this condition overall excitation time \( \tau = N\tau_c \) has to be comparable with the coupling strength, i.e. \( \| \hat{H}_D^{(0)} \| \tau \geq 1 \).

2.4.1.3 Thirty-two pulse sequence

In some cases eight pulse sequence introduced in section 2.4.1.2 is not enough efficient to excite MQ coherences in static solids. As was recently proposed by O.N. Antzukin ([Ant99]) in systems where homonuclear dipole-dipole coupling strength is in the order of chemical shift anisotropy (CSA) or higher, CSA Hamiltonian \( \hat{H}_{CSA} \) interferes with coherence averaging of dipolar Hamiltonian \( \hat{H}_D \) and produce large CSA/dipole-dipole
cross terms in average Hamiltonian. For this reason eight pulse sequence was improved by inserting twenty-four additional π-pulses into each cycle to average out chemical shifts. This pulse sequence is shown in Figure 2.11. Twenty-four pulses are inserted on the time scale $\tau_{echo} = \frac{1}{24} \tau_c$ and cycle time is chosen so that the conditions $||\hat{H}_D|| \tau_c < 1$ and $||\hat{H}_{CSA}|| \tau_{echo} < 1$ are accomplished.

In the next sections two kind of experiments for exciting MQ coherences for studying static solids will be explained. Some of the basic were already made in section 2.3.

## 2.4.2 Separation of MQ coherences

Until now no method was explicitly mentioned for separating of MQ coherences. DQ propagator prepared by time reversal pulse sequences (see e.g. section 2.4.1.2) can excite for the system with more coupled spins also quantum coherences of higher orders. These coherences usually merge together (e.g. in Adamantane in the case of on-resonance excitation). To separate them some methods listed below can be used:

- Separation of quantum-orders by magnetic field variation.

Changing of the static magnetic field $\Delta B_0$ will lead to the change of the Larmor frequency $\Delta \omega_L = \gamma_i \Delta B_0$ of spin $I^i$. In the case of homonuclear $p$-quantum coherence the resulting frequency will be proportional to the sum of $\Delta \omega_L = \sum_{i=1}^{p} \gamma_i \Delta B_0 = p \cdot \gamma I \Delta B_0$. During evolution time $t_1$ such a coherence evolves with different frequencies corresponding to different quantum orders and can be separated by the Fourier transformation. This technique allow us to be on-resonance while exciting

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**Figure 2.11:** Thirty-two pulse sequence used in excitation and reconversion period for exciting MQ coherences in the systems where $||\hat{H}_{CSA}|| \lesssim ||\hat{H}_D||$. The cycle with characteristic time $\tau_c$ consist of eight $\frac{\pi}{2}$-pulses (see also Figure 2.10a) centered about delays $\Delta = \frac{1}{16} \tau_c$ and $\Delta' = 2\Delta = \frac{1}{8} \tau_c$. Twenty-four π pulses (full rectangles), inserted to average out anisotropic chemical shifts on a time scale of $\frac{1}{24} \tau_c$, are centered about times $\frac{2m+1}{48} \tau_c$, $m = 0, 1, 2, \ldots, 23$. The π pulses phases follow the pattern $x, -x, -x, x$, repeated six times.
MQ coherences but requires on the other hand spectrometer, which is able to switch rapidly magnetic field with a good homogeneity. This is usually a big problem and for our spectrometer not applicable.

- **Separation of quantum-orders by off-resonance excitation.**

By off-resonance excitation of MQ coherences, where the resonance offset is defined by $\Delta \omega_{\text{off}}$, the $p$-quantum coherence is shifted by $p \cdot \Delta \omega_{\text{off}}$, written in the density matrix formalism as

$$\hat{\rho}(\tau, t_1) = \sum_p \hat{\rho}^p(\tau, t_1) e^{-ip\Delta \omega_{\text{off}} t_1}. \tag{2.35}$$

This phenomenon can also be used for separating of different orders of coherences. It has to be noted that also line-width of the quantum orders is proportional to the increasing of the order. To resolve higher-quantum orders is than necessary to by strongly out off resonance. On the other hand offsets can influence also average Hamiltonian during excitation and reconversion period and this can cause problems if pulse sequence is not designed to remove these terms. If resonance offsets are very high, compensation in most of the cases does not work properly and unwanted artifacts can appear in the spectrum. This leads to decreasing of the resolution of the particular order of coherence. To get a sufficient resolution a lot of $t_1$ increments has to be done, which rapidly increase measuring time. Some of the examples for separation of quantum orders by off-resonance excitation can be found in M. Munowitz et al. ([Mun87]).

- **Separation of quantum orders by phase change.**

Shifting of the pulses in the excitation period by an angle $\Delta \phi$ from the pulses in the reconversion period leads also to the separation of the quantum orders. $p$-quantum coherence will by then shifted by $p \cdot \Delta \phi$. This effect can by also written using density matrix formalism as

$$\hat{\rho}(\tau, t_1) = \sum_p \hat{\rho}^p(\tau, t_1) e^{-ip\phi}. \tag{2.36}$$

It can be seen that this method provides separation of different orders of coherence even when no evolution during $t_1$ presents (e.g. on-resonance excitation). Either unwanted broadening of the higher orders caused by off-resonance excitation is removed. Changing of the phase allow us to detect maximum $\pm p_{\text{max}}$ orders
of coherence if the size of the increment is determined according to the relation
\[ \Delta \phi = \pi / p_{max} \] ([Yen83]).

In this work the last method for separating of orders of coherences was used. If on-resonance excitation is not possible due to the complicated structure of the sample the second method will also influence the spectrum. In these cases both effects, namely artificial phase change and off-resonance excitation, coexist and \( \Delta \phi \) and \( \Delta t_1 \) must be chosen such that aliasing and overlapping of the coherences is avoided within the available bandwidth equal to \( 1 / \Delta t_1 \).

Two experimental methods used in this work for exiting and detecting different orders of coherences in static solids will be presented. The first one commonly called *time-proportional phase incrementation* (TPPI) and the second one called 'spin-counting' where no evolution during \( t_1 \) take place \( (t_1 = 0) \).

### 2.4.3 TPPI MQ experiment

To separate coherences of different orders *time-proportional phase incrementation* (TPPI) method can be used. How to realize such an experiment is schematically shown in Figure 2.12. This method allows us to excite and resolve desired orders of coherence without introducing the resonance offset. The r.f. pulses of the excitation period are shifted in addition to the r.f. pulses in reconversion period synchronically with incrementing of time \( t_1 \), i.e. \( \phi = \Delta \omega_\phi t_1 \) \( (t_1 = 0, \Delta t_1, 2\Delta t_1, \ldots) \). Fourier transformation of the signal
\[ S_\alpha = \text{Tr} \left\{ \hat{I}_\alpha \hat{\rho} \right\} \]
with respect to \( t_1 \) distributes the different orders over the bandwidth in \( \omega_1 \) dimension equal to \( \frac{1}{\Delta t_1} \). Adjacent orders are therefore separated by the apparent offset frequency \( \Delta \omega_\phi = \frac{\Delta \phi}{\Delta t_1} \). The number of orders detected is \( \pm p_{max} \) and is determined by the size of the phase increment so that \( \Delta \phi = \frac{\pi}{p_{max}} \). It means e.g. for \( p_{max} = 4 \) maximum four quantum orders of coherences can be seen in the spectrum. Important is also to chose \( \Delta t_1 \) and \( \Delta \phi \) so that all signals from different coherence orders fit into the available bandwidth \( (\frac{1}{\Delta t_1}) \) to prevent aliasing and overlapping of the lines in the spectrum.

The demonstration of the excitation of MQ coherences was made on the polycrystalline Adamantane \( (C_{10}H_{16}) \). Adamantane at room temperature forms a plastic crystal in which the nearby spherical molecules tumble rapidly and isotropically. The motion averages all intra-molecular dipolar couplings to zero, but does not eliminate inter-molecular couplings. However, the motion leaves only one distinct coupling between every pair of molecules,
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2.4. Static MQ experiment

Figure 2.12: General form of pulse sequences for 2D MQ NMR spectroscopy for static solids. Separation of p-quantum orders is accomplished by shifting the excitation pulses by an amount $\phi = \Delta \omega \phi t_1$ (TPPI, see text). Time reversal is made by shifting excitation pulses by $\frac{\pi}{2}$ during reconversion period: $\hat{H}_{\text{rec}} = (\hat{H}_{\text{exc}})_{\phi=\pi/2} = -\hat{H}_{\text{exc}}$ (see also section 2.3.1). The delay $\tau_0$ between reconversion period and detection pulse can be included to allow dephasing of undesirable coherences. This delay should be not so long to prevent unwanted magnetization exchange during this time.

drayer reducing the Adamantane molecule to a point dipole source containing 16 spins. The molecules pack into face-centered-cubic lattice, with each Adamantane molecule surrounded by 12 neighbours at a distance of 6.60 Å, 6 more at 9.34 Å, and additional 16 at 11.4 Å ([Now45]).

Experimental results of $^1$H MQ spectrum of polycrystalline Adamantane can be found in Figure 2.13. Experiment was made with eight pulse sequence presented in Figure 2.10b (see page 42) which was applied during excitation and reconversion period. Separation of different orders has been accomplished by TPPI, so that $\Delta \phi$ and $\Delta t$ were chosen as $\Delta \phi = 8^\circ$ and $\Delta t_1 = 0.1 \mu s$, respectively, to prevent aliasing and overlapping of adjacent coherence orders. The basic eight pulse sequence cycle $\tau_c$ was repeated $N = 8$ times to get the overall excitation time $\tau = 384 \mu s$. Time spectrum was transformed by the conventional Fourier transformation to get the resulting spectrum shown in Figure 2.13. Since coherences of $+p$ and $-p$ are equally probable, the spectrum is naturally symmetric about $p = 0$. To obtain then all the information available only one-half of the spectrum is necessary to be displayed. Up to 22 even order coherences can be seen.

In some cases we are not interested to have the information about the line shapes of MQ coherences and so time evolution between excitation and reconversion pulses (see Figure 2.12) can be simply omitted ($t_1 = 0$). This kind of experiment will be presented in the next section.
Figure 2.13: 400MHz $^1$H multiple quantum spectrum of polycrystalline Adamantane at room temperature. Eight pulse sequence (Figure 2.10b) was used to excite up to 22 ($p_{\text{max}} = 22$) order of coherences with excitation time $\tau = 384 \mu s$. The basic cycle time $\tau_c$ was chosen 48 $\mu s$ ($t_p = 3.2 \mu s$, $\Delta = 0.8 \mu s$, and $\Delta' = 4.8 \mu s$). Separation of different orders of coherences has been made by TPPI (for details see text). A delay of $\tau_0 = 1.6 \, ms$ was included after reconversion period to allow unwanted transients to decay away from the spectrum. The $z$-component of magnetization is monitored by $\frac{\pi}{2}$ detection pulse with the phase $\pm x$ which is cycled to remove spectrometer offset.

2.4.4 Spin counting MQ experiment

Time reversal MQ experiment shown in the previous section where TPPI method for exciting coherences of very high orders has been used, is very time consuming. One has to realize enough time $t_1$ increments to get the sufficient resolution of the adjacent MQ coherences. In such an experiment the important information about growing of the spin clusters is contained in the integrated intensities of the MQ orders, rather than in the different frequencies occurring within each order. Shykind et al. ([Shy88]) showed that even integration of individual coherence orders is in most of the cases not necessary for obtaining the cluster sizes. In these cases time evolution from MQ experiments can be simply omitted ($t_1 = 0$). Measuring time than will be rapidly decreased from e.g. 12 hours (with TPPI) to couple of tens minutes (without TPPI). This kind of experiment will be called "spin counting" experiment in this work (similar like in literature).

The basic scheme of MQ spin counting experiment is shown in Figure 2.14. Reconversion period follows immediately excitation period without supplementary evolution time $t_1$. The separation of quantum orders is made by changing of r.f. pulse phases during the excitation period while phases of the r.f. pulses in the reconversion period are holding
Design of the spin counting experiment. Pulses during excitation period are shifted according the rule $\phi = m \cdot \Delta \phi$ with $m = 0, 1, \ldots, q - 1$ in the same way like in TPPI experiment (more details can be found in the text and in the description under Figure 2.12).

constant. The phase change about $\phi$ of the r.f. pulses will lead to the $p \cdot \phi$ phase change for desired $p$-quantum order which can be written using density matrix formalism as (see e.g. equation (2.36))

$$\hat{\rho}(\tau) = \sum_p \hat{\rho}^p(\tau) e^{-ip\phi}. \quad (2.37)$$

Similar like in TPPI experiment (see section 2.4.3) the phases of excitation pulses will be changed as $\phi = m \cdot \Delta \phi$ where $\Delta \phi = \frac{\pi}{p_{\text{max}}}$ is determined by the maximum $p_{\text{max}}$ quantum order of visible coherences in the spectrum. Because the signal is strictly periodic with the period $2\pi$ it is enough to vary the phase $\phi$ only in the range $0 \ldots 2\pi$. Hence number of phase increments $q$ $(m = 0, 1, \ldots, q - 1)$ has to be chosen as $q = k \frac{2\pi}{\Delta \phi}$ where $k$ $(k = 1, 2, \ldots)$ represents periodicity. Additionally, to realize the numerical Fourier transformation (fast fourier transform, FFT) of the periodic function, $k$ and $p_{\text{max}}$ have to fulfill the condition $k \cdot p_{\text{max}} = 2^j$ $(j \in \mathbb{N})$ to get the correct results. Experimental results of spin counting experiment can be found in section 3.5.2.

### 2.5 MAS MQ experiment

On contrary to the static MQ experiments MAS provides much higher spectral resolution for studying abundant spins in solids. MAS effectively suppress dipole-dipole interaction (see section 1.6) as well as chemical shift anisotropy (CSA) interaction ([Meh83]). Three possible strategies can be used while combining more quantum NMR methods with rotation of the sample at magic angle:

- **quasi-static excitation**: Conventional static multiple-pulse sequences (see sections 2.2 and 2.4.1) can be used to excite MQ coherences with the limitation for excitation time $\tau \leq 0.5\tau_r$. This strong condition where excitation time can not exceed
half of the rotor period $\tau_r$, limits the use of this method for slow spinning speeds. Dipolar coupling is in this case still not sufficiently averaged by MAS ($\omega_r \leq ||\hat{H}_D||$) so effective high resolution is not achieved. This method leads to the compromise between an optimal spectrum resolution and the enough long excitation time $\tau$ for detecting higher MQ coherences. Using quasi-static method MQ coherences in liquid samples can be excited with the help of e.g. three pulse sequence.

- **MAS synchronized excitation:** If the spinning frequency becomes high enough to resolve averaged dipolar interaction ($\omega_r \gg ||\hat{H}_D||$) time reversal pulse sequences used for static samples (see section 2.4.1) will not more effectively excite MQ coherences in solids. MAS during excitation and reconversion periods causes a ‘self-time reversal’, and MQ coherences disappear after each full rotor period. The solution suggested by Meier and Earl ([Mei86]) to prevent this process of ‘self-time reversal’ involves phase switching the original pulse sequences every half rotor period. The average Hamiltonian in a multiple-pulse sequence has been manipulated such that its sign has been changed synchronously with the spinner rotation. However, this method is necessarily limited to situations in which the spinning rate is sufficiently slow to allow at least two cycles of the multiple-pulse sequence to fit into a single rotor period ($2\tau_c \leq \tau_r$). This method is therefore restricted to samples with small dipolar couplings e.g. for studying labelled pairs of $^{13}$C nuclei ([Mei87]).

- **fast MAS excitation (rotor synchronized):** An alternative approach to the second method proposed by Meier and Earl will be used in this work where cycle time $\tau_c$ is a whole number of rotor periods ($\tau_c = n \cdot \tau_r; n = 1, 2, \ldots$). This leads to MQ experiments suitable even at very fast MAS speeds. In some cases these high spinning speeds are required to obtain high-resolution spectra for abundant spins in solids. Under the fast MAS conditions ($||\hat{H}_D|| \ll \omega_r$) where spectral lines are successfully narrowed dipole-dipole coupling is averaged to zero $\langle \hat{H}_D \rangle \rightarrow 0$ which act like a disadvantage. Consequently recoupling of the dipolar coupling is necessary. This can be done by a rotor synchronized recoupling pulse sequences like e.g. DRAMA, BABA, C7, \ldots (see section 2.5.1). For strong coupled spin systems ($\omega_D/2\pi \gg 10$ kHz) recoupling pulse sequences are already not so often used because higher terms of effective average Hamiltonians reduced by this sequences in the

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$^6$This is a consequent of the fact that the dipolar interaction has an isotropic value of zero.
Magnus expansion (see section 1.3) can have unexpected effects during recoupling. For rigid solids where $\omega_D/2\pi \approx 50$ kHz this method is not more useful because of the limitation in MAS spinning speeds (up to now $\omega_r/2\pi \approx 40$ kHz have been reached). Due to the synchronization of the r.f. pulses to the spinning frequency the excitation time $\tau$ can be only the whole number of the rotor period $\tau_r$ (except C7) which is in some cases also disadvantage.

In the following part we will introduce some recoupling pulse sequences which are suitable for qualitative measuring of dipolar couplings for abundant spins in solids. Some of them can be effectively used for monitoring the evolution of the spin clusters under MAS as will be shown in section 2.5.3.

### 2.5.1 Recoupling pulse sequences

In recent years a lot of recoupling pulse sequences were developed for measuring dipole-dipole couplings under MAS for solids. High spinning speeds are in most of the cases prerequisite for obtaining high resolution spectra in solids. Recoupling pulse sequences can be divided in principle into two categories.

The first one is dealing with high power r.f. pulses which are for calculating average Hamiltonian operators of particular pulse sequence described via $\delta$-pulses. Such a treatment was in more details introduced in section 2.4.2 for static solids. Duration of the r.f. pulses $t_p$ has to be for these pulse sequences much smaller compared to the rotational period $\tau_r$. Consequently with increasing spinning speeds higher r.f. powers and shorter r.f. pulses are required. This is the strong demand for a very good spectrometer if spinning speeds exceed $f_r > 20$ kHz.

In the second category are recoupling pulse sequences working with relatively long r.f pulses (spinlock-pulses) where duration of the pulses is fixed to the rotor period. In other words, the r.f. field strength witch leads to the precession of the spins $I$ in the rotating frame with the angular frequency $\omega_1 = \gamma I B_1$ has to be a whole number of the rotational angular frequency $\omega_r$ ($\omega_1 = n \cdot \omega_r; \ n = 1, 2, \ldots$). For calculating average Hamiltonians, periods of r.f. pulses where toggling-frame Hamiltonians\footnote{Frame where Hamiltonians of the spin system are expressed in the interaction frame of the r.f. field (see also equation (1.45)).} are changing continuously have to be assumed. In general these pulse sequences are sensitive to the homogeneity of the r.f. field as well as to the sufficiently fast changing of the phases between pulses.
Figure 2.15: Rotor synchronize DRAMA pulse sequence. a) Original pulse sequence which leads to the recoupling of the dipolar coupling under MAS. b) The second variant where DQ average Hamiltonian is prepared after finishing of full rotor cycle $\tau_r$ ($\tau_1 = \tau_r/4$, $\tau_2 = 2\tau_1$). Overall excitation time $\tau$ can be manipulated through integer number $N$ ($\tau = N\tau_r$).

Their efficiency is generally higher (e.g. for C7 [Lee95] or for MELODRAMA [Sun94]) than for that with ‘δ-pulses’.

We will concentrate in this work to the MQ recoupling pulse sequences working with short ‘δ-pulses’ like DRAMA or BABA, and for that with spin-lock pulses like C7 or POST-C7 ([Hoh98]). In the next part these pulse sequences will be explained in more details.

2.5.1.1 DRAMA

The oldest pulse sequence which was able to recover dipole-dipole coupling under fast MAS was DRAMA (dipolar recovery at the magic angle) proposed by R. Tycko and G. Dabbagh [Tyc90]. It is shown in Figure 2.15a. Because this simple version consisting of two 90°-pulses was not able to efficiently recover homonuclear dipolar coupling several improvements were made in the case of $^{13}$C NMR spectroscopy ([Tyc91, Tyc93]). Extending of the original pulse sequence by two additional pulses shifted by 90° phase from the original ones and positioning them at the beginning and at the end of the cycle interval as it is shown in Figure 2.15b even quantum order selective dipolar Hamiltonian can be derived. This pulse sequence was successfully applied for proton $^1$H systems under fast MAS by H. Geen et al. [Gee94]. It was shown ([Gee95]) that it generates ‘pure’ double quantum (DQ) average Hamiltonian for homonuclear dipole-dipole coupling in samples where CSA and resonance offsets can be neglected.

Assuming isolated spin pair coupled via dipole-dipole interaction toggling-frame states for DRAMA can be determined as can be seen from Figure 2.16 (more details see section 2.4.1.1). Because the geometrical part $R^{12}_{0,0}$ of the dipolar Hamiltonian
(equation (1.60)) becomes time dependent under MAS as was shown in equation (1.74) we will define for better understanding of the pulse sequence rotor-modulated functions

\[ F_{S1} = \sin(\omega_r t) \quad F_{C1} = \cos(\omega_r t) \quad F_{S2} = \sin(2\omega_r t) \quad F_{C2} = \cos(2\omega_r t) \]  \hspace{1cm} (2.38)

These functions can be used for an intuitive description of the modulation of a particular Hamiltonian by equation (1.74) under MAS. Combining now toggling frame Hamiltonians prepared after each pulse in DRAMA pulse sequence with the rotor modulated functions it can be directly shown that DQ average Hamiltonian (more details see section 2.4.1)

\[ \hat{H}_{D, \text{DRAMA}}^{(0)} = \frac{1}{2} \left( \hat{H}_{xx} - \hat{H}_{yy} \right) \]  \hspace{1cm} (2.39)

is recoupled in \( F_{C1} \) component (see Figure 2.16). It can be simply proven that average Hamiltonian presented in equation above represents 'pure' DQ operator for a system with two coupled spins. It is clear that this simple description can by used only for the intuitive understanding of the pulse sequence. Detailed theoretical analysis made by R. Graf et al. [Gra97b] (can be proven by assuming equations (1.74), (1.61), (1.59) and (1.45), (1.54)) shows that zero-order average Hamiltonian for homonuclear coupling in the limit of \( \delta \)-pulses is given by

\[ \hat{H}_{D, \text{DRAMA}}^{(0)} = - \sum_{i<j} \frac{3}{\pi \sqrt{2}} d_{ij}^{II} \sin(2\theta_{ij}) \cos(\psi_{ij} + \omega_r t^0) \left( \hat{T}_{2,x}^{ij} + \hat{T}_{2,-x}^{ij} \right) \]  \hspace{1cm} (2.40)

\( d_{ij}^{II} \) represents the dipolar coupling constant defined by equation (1.27) and \( \hat{T}_{2,x}^{ij} \) are irreducible tensor operators (see Appendix A) describing ±DQ coherence. The Euler angles \( (\varphi_{ij}, \theta_{ij}, \psi_{ij}) \) relate the principal axes of dipolar coupling tensor to the reference frame fixed on the rotor (more details see section 1.6). \( \omega_r t^0 \) describes modulation of the \( \psi_{ij} \) angle with the initial position of the rotor represented by time point \( t^0 \) at which the pulse sequence is initiated. It is especially important during reconversion period.

Introducing CSA or resonance offset terms written in the general form \( \hat{H}_z = \Omega \hat{I}_z \), zero order average Hamiltonian can be calculated for these interaction. Non zero contribution to the average Hamiltonian will be found only in the \( F_{C1} \) component of the rotor-modulated function (see Figure 2.16) and it can be written as

\[ \hat{H}_{\Omega, \text{DRAMA}}^{(0)} = \frac{1}{2} \Omega \left( \hat{I}_x + \hat{I}_y \right) \]  \hspace{1cm} (2.41)

This term represents an unwanted contribution to the signal. This version of DRAMA therefore does not lead do the correct results if CSA or resonance offset can not be neglected
Figure 2.16: DRAMA pulse sequence reflected by the four rotor-modulated functions (see equation (2.38) and equation (1.74)). Toggling frame Hamiltonians for each interval between pulses are indicated for CSA (or resonance offsets) and dipolar interaction respectively. These states are weighted by the areas under the rotor-modulated function for the time during which they are present. Positive or negative contributions of the toggling Hamiltonians to the average Hamiltonian are indicated with sign $+$ or $-$. In this way, a non-vanishing DQ average Hamiltonian $\hat{H}_{DQ} = \hat{H}_{xx} - \hat{H}_{yy}$ is created only in $F_{C1}$ component. As can be seen average Hamiltonian is in other components cancelled. CSA interaction (or resonance offset terms) are not removed from the average Hamiltonian a can contribute to the resulting spectrum (more details see text).

(e.g. if sample has more than one isotropic components). Several attempts to compensate these unwanted signal were made for DRAMA pulse sequence ([Tyc91, Tyc93]). They lead to the complicated pulse sequences with long cycle times which are in experiment hard to handle. It will be shown that another compensated pulse sequences like BABA and C7 are much more efficient.
Figure 2.17: Rotor synchronize BABA pulse sequence. a) Original version where timing is set to \( \tau' = \tau_r/2 \) in the \( \delta \)-pulses limit. b) Improved version where resonance offsets and CSA are averaged out in the zero-order average Hamiltonian during two full rotor periods \( 2\tau_r \). Overall excitation time can be manipulated through integer number \( N \) \((\tau = N \cdot \tau_r \text{ or } \tau = N \cdot 2\tau_r)\).

### 2.5.1.2 BABA

BABA pulse sequence has been developed on the basis of Meier-Earl [Mei86] synchronization scheme setting the r.f. pulses back-to-back. Initially the pulse sequence \((-\hat{\Delta} - (\frac{\pi}{2})_x - \tau' - (\frac{\pi}{2})_{-x} - \Delta - (\frac{\pi}{2})_y - \tau' - (\frac{\pi}{2})_{-y} - \hat{\Delta})\) acting in the presence of fast MAS has been regarded [Som95]. Considering \( \delta \)-pulses DQ average Hamiltonian is prepared for this pulse sequence if the synchronization is accomplished as \( \tau' = \tau_r/2 \) and \( \Delta \to 0 \). The basic version of BABA pulse sequence is shown in Figure 2.17a. As will be shown later this simplest version acting on the one rotor cycle does not remove CSA terms and is also sensitive to the resonance offsets like DRAMA pulse sequence. Improved version proposed by Feike et al. [Fei96a] which is shown in Figure 2.17b can solve this problem. Full compensation can be achieved during two rotor cycles.

Similar like for DRAMA (section 2.5.1.1) pulse sequence the zero order average Hamiltonian in the Magnus expansion can be intuitively estimated using toggling frame states modulated with the rotor functions defined by equations (2.38). Toggling frame Hamiltonians for basic version of BABA pulse sequence are shown in Figure 2.18. It can be simply seen from the drawing that zero-order average Hamiltonian for homonuclear dipolar coupling in the \( \delta \)-pulse limit \((\Delta = 0, \tau' = \tau_r/2)\) is found in the \( F_S1 \) rotor-modulated function as

\[
\hat{H}^{(0)}_{D,BABA} \approx \frac{1}{2} \left( \hat{H}_{yy} - \hat{H}_{xx} \right).
\] (2.42)

It is the same average Hamiltonian as for DRAMA (see equation (2.39)) pulse sequence (except sign\(^8\)). More detailed calculations shows the exact value of the zero order average

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\(^8\)Sign is not important in this intuitive approximation. It can be changed by proper time integration of the geometrical function \( R_{2,0}(t) \) (see equation (1.74)) over the full cycle of the pulse sequence.
Figure 2.18: Basic version of BABA pulse sequence reflected by four rotor-modulated functions (see also description under Figure 2.16). Non vanishing DQ average dipolar Hamiltonian $\hat{H}_{DQ} = \hat{H}_{yy} - \hat{H}_{xx}$ is created in $F_{S1}$ rotor function. In other components it is averaged out. CSA terms or resonance offsets written in the general form $\hat{H}_z = \hat{I}_z$ can contribute to the resulting zero-order average Hamiltonian also in $F_{S1}$ rotor function and can be written as $\hat{H}_z^{(0)} = -\frac{1}{2}\Omega (\hat{j}_x + \hat{j}_y)$. Shaded areas represent error term arising from finite switching delays $\Delta$ between pulses in the case of $\delta$-pulses (more retails see text).

Hamiltonian in the $\delta$-pulse limit approximation ([Fei96a]) as

$$\hat{H}_{D,BABA}^{(0)} = -\sum_{i<j} \frac{3}{\pi \sqrt{2}} d_{ij} \sin(2\theta_{ij}) \cos(\psi_{ij} + \omega_i t^0) \left( \hat{T}_{2,2}^{ij} + \hat{T}_{2,-2}^{ij} \right). \quad (2.43)$$

This result exactly correspond to zero-order average Hamiltonian for DRAMA pulse sequence (equation (2.40)). Both pulse sequences then excite even order MQ coherences with the same efficiency. This is limited to the short excitation times ($1 - 2$ rotor periods) and the samples with the small chemical shifts ([Fei96b]). An advantage of BABA pulse
sequence is in the second variant (Figure 2.17b) where CSA and resonance offsets are compensated (detailed analysis see [Fei96a]). Error terms arising from finite pulse lengths can be compensated by shifting of the all pulses in BABA pulse sequence about 180° in the next full cycle. This lead to the reducing of the zero-order average Hamiltonian presented in equation (2.43) by the small amount. Therefore, very short r.f. pulses are prerequisite for both BABA and DRAMA pulse sequences.

We will now shortly discuss the problem of the switching of the phases between pulses for BABA pulse sequence. It is known that such a delay Δ is needed for each pulse after setting the phase of the pulse until the phase settle. Design of the BABA pulse sequence force us to think about this problem, which was not the case of DRAMA pulse sequence where no pulses were so close together. Error contributions to the zero-order average Hamiltonian for the original version of BABA pulse sequence are representing by the shadow areas of each rotor-modulated function (see Figure 2.18). For simplicity δ-pulses has been assumed. As can be seen from the drawing non-zero component to the average Hamiltonian appear only from $F_{C2}$ component of the rotor-modulated function. It can be calculated in the limit of $Δ ≪ τ_r$ that contributions from the finite switching delay (FSD) to the homonuclear dipolar Hamiltonian have the form:

$$\hat{H}_{D,FSD}^{(0)} \approx \frac{3Δ}{τ_r} \hat{H}_{zz}.$$  \hspace{1cm} (2.44)

Error terms to the zero-order CSA (or resonance offsets) average Hamiltonian can also be calculated by

$$\hat{H}_{Ω,FSD}^{(0)} \approx \frac{Δ}{τ_r} \left(2Ω\hat{I}_z + Ω\hat{I}_y - Ω\hat{I}_x \right).$$  \hspace{1cm} (2.45)

Same analysis can be applied for the full compensated BABA pulse sequence shown in Figure 2.17b. It will be found that contributions to the zero-order homonuclear dipolar Hamiltonian and CSA (or resonance offsets) average Hamiltonian can be written

$$\hat{H}_{D,FSD}^{(0)} \approx \frac{6Δ}{τ_r} \hat{H}_{zz} \quad , \quad \hat{H}_{Ω,FSD}^{(0)} = 0,$$  \hspace{1cm} (2.46)

respectively. Full compensation of the CSA terms and resonance offsets is directly seen from equation above even when small phase-switching delays Δ are presented. It is important to note that homonuclear contribution to the average Hamiltonian was not removed but doubled. This error is than increased proportionally with increasing number of cycles N. It can not be removed even by shifting of the phases of the pulses by 180° in the
next full cycle which eliminates the error terms arising from finite pulse length. Beside
the fact that this effect is additive it is very small because $\Delta < 0.5\, \mu s$ in commercial
spectrometers and even for very high spinning speeds $f_r = 40\, kHz$ can be neglected. In
addition it contribute to the zero-quantum coherence (from equation 2.44: $\hat{H}_{zz} \approx \hat{T}_{2,0}$)
and can by separated from the DQ spectra by TPPI as will be shown in sections 2.5.2 and 2.5.3.

2.5.1.3 C7

C7 pulse sequence belongs to the second category of the recoupling pulse sequences. It
works with relatively long r.f. pulses (spinlock-pulses) with duration fixed to the rotor
period despite $\delta$-pulses sequences like DRAMA and BABA. It is a full compensated pulse
sequence first time proposed by Y.K. Lee et al. [Lee95]. The name of the C7 is derived from
the sevenfold-symmetric phase shift scheme acting on the two rotor periods $2\tau_r$. It provides
homonuclear dipolar recoupling with better efficiency than previous pulse sequences and is
much less sensitive to higher resonance offsets and CSA terms. It was shown by Y.K. Lee
et al. that its efficiency is around two times higher for $^{13}C$ systems with large chemical
shifts (both isotropic and anisotropic) than DRAMA pulse sequence.

The $^1H$ version of C7 pulse sequence is shown in Figure 2.19. Seven elements ($C_{\phi'}$)
are timed to occupy two rotational periods. Neighbouring elements differ in phase by
$\Delta \phi' = \frac{2\pi}{7}$ always rotating in the same sense. In the simplest version ([Lee95]) each element
$C_{\phi'}$ consists of two r.f. pulses (see Figure 2.19a), both with r.f. phases differing by $\pi$. The
strength of the r.f. field $B_1$ has to be adjusted in order to be equal seven times the spinning
frequency $\omega_{B_1} = 7\omega_r$. This condition leads to the $2\pi$ flip angle of the r.f. pulse. Then,
each element can be described in the conventional notation by $C_{\phi'} = (2\pi)_{\phi'}(2\pi)_{\phi'+\pi}$. The
duration of the $C_{\phi'}$ element can be simply estimated as $\frac{2\pi}{\omega_r}$. As was shown in reference
[Lee95] zero-order homonuclear dipolar average Hamiltonian for C7 can be calculated as

$$\hat{H}_{D,C7}^{(0)} = \sum_{k<l} \left\{ \omega_{kl} \hat{T}_{2,2}^{kl} + \omega_{kl}^* \hat{T}_{2,-2}^{kl} \right\}, \tag{2.47}$$

where

$$\omega_{kl} = \frac{343(i + e^{i\pi/14})}{520\pi \sqrt{2}} \ d_{kl}^{1H} \sin(2\theta_{kl}) e^{i(\omega_r t^0 - \psi_{kl})}. \tag{2.48}$$

$^9$We will change indexation for this section from traditional $ij$ to $kl$ to clearly distinguish between
indexes and imaginary number $i$. 
2.5. MAS MQ experiment

Figure 2.19: C7 pulse sequence. Seven fold-symmetric r.f. pulse scheme timed on two rotor periods $2\tau_r$ leads to the compensation of all unwanted interactions (more details see text). Each element with duration $\tau_c = 2\tau_r/7$ differs in the phase from the previous one by $2\pi/7$. In the basic version a) each element consists of two $2\pi$ r.f. pulses differing in the phase by $\pi$. The second version b) called POST C7 having three pulses in the base element is even much less sensitive to resonance offsets (see text). Overall excitation time $\tau$ can be changed by integer number $N$ ($\tau = N \cdot 2\tau_r$). It was shown by [Lee95] that even incomplete C7 cycles ($\tau = n \cdot \tau_c$, $n \geq 7$) generates DQ average Hamiltonian. The full compensation is established only after full sevenfold cycle ($n = 7N$).

Detailed explanation of the symbols in equation above can be seen under equation (2.40). $t_0$ represents the time point at which the pulse sequence is initiated. It is especially important during reconversion period because it indicates the phase of the DQ Hamiltonian. On contrary to DRAMA and BABA pulse sequences magnitude of zero-order dipolar average Hamiltonian (equation (2.48)) does not depend on the angle $\psi_{kl}$ and leads to the higher efficiency of C7 pulse sequence especially in powders. C7 shown in Figure 2.19a compensate isotropic resonance offsets and r.f. inhomogeneity to first-order in the Magnus expansion.

In Figure 2.19b the second variant of C7 is shown. It was named as POST C7 [Hoh98] (permutationally offset stabilized C7). Theoretical and experimental analysis performed by M. Hohwy et al. [Hoh98] shows that POST C7 is even less sensitive to the resonance offsets as original version of C7. POST C7 consist of three pulses in the base element

$C_{\phi'} = (\frac{\pi}{2})_{\phi'} (2\pi)_{\phi'} + \pi (\frac{3\pi}{2})_{\phi'}$ (see Figure 2.19b). The zero-order homonuclear dipolar average Hamiltonian of POST C7 is identical with C7 (see equations (2.47)–(2.48)). It is supposed to eliminate isotropic resonance offsets up to fourth-order in the Magnus expansion.
expansion and isotropic resonance offsets/r.f. inhomogeneity up to third-order. It also removes the effects of CSA in the zero-order expansion similar like C7.

Comparing C7 with other recoupling pulse sequences of the same kind like HORROR (homonuclear rotary resonance, [Nie94]) it provides better experimental results with higher efficiency. The basic version of C7 was also used in $^{31}$P NMR spectroscopy to obtain high resolution spectra in powders ([Dol97]). Besides POST C7 other compensation schemes were designed [Rie98] which might lead to even greater efficiencies. In this work most of the experiments were performed with POST C7 because of sufficiently high compensation.

2.5.2 Two-dimensional MQ experiment

General form of the pulse sequence scheme for two-dimensional (2D) MQ experiment under MAS is shown in Figure 2.20. It is nearly identical with the design of 2D MQ experiment for static solids (see Figure 2.12) with an exception of rotor synchronization for the pulses during excitation and reconversion period. Synchronization of the detecting pulse ($n_0\tau_r$) is not a prerequisite for this kind of experiment, but it was used in this work.

Separation of different orders of coherence is accomplished by TPPI similar like in section 2.4.3. Time reversal during reconversion period is made by shifting of the r.f. pulses by $\frac{\pi}{2}$ in comparison to the pulses acting during excitation period (for details see section 2.3.1). Pulse sequences used in this work can be described by average Hamiltonian representing ‘pure’ DQ operator for the two spins-$\frac{1}{2}$ system and can be written in the general form as (see also sections 2.5.1.1 - 2.5.1.3)

$$\hat{H}_{DQ} = \sum_{i<j} \left\{ \omega_{ij}(\theta, \psi, t^0) \hat{T}_{ij}^{2,2} + \omega_{ij}^*(\theta, \psi, t^0) \hat{T}_{ij}^{2,-2} \right\}. \quad (2.49)$$

The complex term $\omega_{ij}$ corresponds to the amplitude and to the phase of the DQ Hamiltonian. It depends on Euler angles ($\theta, \psi$) and on the starting time point $t^0$ of the particular pulse sequence (see e.g. equation (2.40)). DQ Hamiltonian shown in equation (2.49) can excite even order of coherences under ideal conditions ([War80]).

TPPI in 2D MQ experiment (Figure 2.20) is performed by the phase change of the r.f. pulses during excitation period synchronically with increasing evolution time $t_1$ as: $\phi = \phi(t_1) = \Delta \omega_0 t_1$ ($t_1 = 0, \Delta t_1, 2\Delta t_1, \ldots$). Such a phase change gives rise to the transformation of the DQ spin operator $\hat{T}_{2,\pm 2}$ as ([Ern87, SR94])

$$e^{-i\phi \hat{I}_z} \hat{T}_{2,\pm 2} e^{i\phi \hat{I}_z} = e^{\pm i2\phi} \hat{T}_{2,\pm 2}. \quad (2.50)$$
Figure 2.20: Design of the 2D single channel (in \( t_1 \) dimension) MQ experiment under MAS. Rotor synchronized pulse sequences like DRAMA, BABA and C7 can be used in the excitation and reconversion periods, respectively. \( n \) represent symbolically rotor synchronization \((n = 1, 2, \ldots)\). Separation of different orders is made by TPPI (see text). A period \( n_0 \tau_r \) \((n_0 = 1, 2, \ldots)\) is inserted between the reconversion and detection period to allow undesired coherences to dephase.

Simply speaking it evokes changing of the phase for DQ coherence by an angle \( 2\phi \). Inserting equation (2.50) in to equation (2.49) the DQ average Hamiltonian during excitation period is derived and is dolds

\[
\hat{H}^{\text{exc}}_{DQ} = \sum_{i<j} \left\{ \omega_{ij}(\theta, \psi, t^0 = 0) e^{-i2\phi(t_1)} \hat{T}_{2,2}^{ij} + \omega_{ij}^*(\theta, \psi, t^0 = 0) e^{i2\phi(t_1)} \hat{T}_{2,-2}^{ij} \right\}. \tag{2.51}
\]

Initial position of the rotor has for \( \hat{H}^{\text{exc}}_{DQ} \) no importance and can be set to zero: \( t^0 = 0 \). The response of the spin system to the excitation Hamiltonian (equation (2.51)), in the case of spin pairs, is simplified by the fact that DQ coherence does not evolve under the influence of the dipolar coupling (see also equation (2.11) and equation (1.75)) since

\[
[\hat{H}_D(t), \hat{H}^{\text{exc}}_{DQ}] = 0.
\]

The influence of the sample rotation to the resulting signal is described by reconversion Hamiltonian. Its DQ form where rotor modulation is present during evolution time \( t_1 \) is written as (see also equations (2.40), (2.43), (2.47))

\[
\hat{H}^{\text{rec}}_{DQ} = -\sum_{i<j} \left\{ \omega_{ij}(\theta, \psi, t^0 = t_1) \hat{T}_{2,2}^{ij} + \omega_{ij}^*(\theta, \psi, t^0 = t_1) \hat{T}_{2,-2}^{ij} \right\}. \tag{2.52}
\]

The minus sign in the prefactor of this Hamiltonian is the result of the \( \frac{\pi}{2} \)-phase shift of the pulses of the reconversion period compared with the excitation period.

This kind of experiment, where pulse sequence is characterized by the DQ operator excites even-order coherences which are distributed over the bandwidth in \( \omega_1 \) dimension equal to \( \frac{1}{2T_1} \). TPPI separate adjacent orders of coherences by the apparent offset frequency \( \Delta \omega_\phi = \frac{\Delta \phi}{2T_1} \), where the phase increment is: \( \Delta \phi = \frac{\pi}{p_{\text{max}}} \). The highest quantum order detected is \( \pm p_{\text{max}} \). In addition each order is modulated by the spinning frequency \( \omega_r \)

\(^{10}\)For neighbouring even quantum orders is the offset frequency than \( 2 \cdot \Delta \omega_\phi \).
which leads to the supplementary offset to the \( p \)-quantum coherence offset (\( p \cdot \Delta \omega_\phi \)). This results in the sideband spectrum for each \( p \)-quantum order (especially for DQ sideband pattern see section 3.2). This can lead to the very complicated spectrum where a lot of sidebands originating from the neighboured quantum orders overlap. Care has to be taken to choose proper \( \Delta t_1, \Delta \phi \) and spinning frequency \( \omega_r \) to prevent overlapping and aliasing of the sidebands from different orders. Selective excitation ([War79, War80, War81]) or DQ filtering (see section 4.3) may be the solution to this problem.

Due to the fact that 2D MAS experiment is quite time consuming and for strong coupled systems of spins-\( \frac{1}{2} \), \( \Delta \phi \) (\( p_{\text{max}} \)) has to be chosen small (high) enough which decrease the resolution of the Fourier spectrum and thus more \( t_1 \) increments has to be made, we where concentrated to systems with relatively weak couplings (see section 3.3).

### 2.5.3 Spin counting MQ experiment

Spin counting experiment already described in section 2.4.4 can be realized under MAS conditions. It is particularly important for systems with strong couplings where also higher order coherences may be expected and line shapes are not of interest. It was shown by H. Geen et al. [Gee99] that such an experiment can be used for studying spin clusters under MAS on Adamantane. Their results show an agreement with the result from the traditional experiment provided on static solids [Bau85] where eight pulse sequence (see section 2.4.1.2) was used.

The general scheme of MQ spin counting experiment is shown in Figure 2.21. Evolution time \( t_1 \) between excitation and reconversion period is simply omitted (\( t_1 = 0 \)). Excitation and reconversion periods are strictly rotor synchronized in the same way like in section 2.5.2. Phase of the r.f. pulses acting during excitation period are changed in the similar way like in TPPI experiment \( \phi = m \cdot \Delta \phi \), where \( \Delta \phi = \frac{\pi}{p_{\text{max}}} \) is related to the maximum observed coherence order \( p_{\text{max}} \) in the spectrum. DQ average Hamiltonian during excitation period for pulse sequences like DRAMA, BABA and C7 (see sections 2.5.1.1, 2.5.1.2 and 2.5.1.3) according to their general form presented by equation (2.49) can be written as (see also equation (2.50))

\[
\hat{H}_{\text{DQ}}^{\text{exc}} = \sum_{i<j} \left\{ \omega_{ij}(\vartheta, \psi, t^0 = 0) e^{-i2m\cdot\Delta \phi \hat{T}_{2,2}^{ij}} + \omega_{ij}^*(\vartheta, \psi, t^0 = 0) e^{i2m\cdot\Delta \phi \hat{T}_{2,2}^{ij}} \right\}. \tag{2.53}
\]

DQ coherence will be thus shifted by the amount \( 2\Delta \phi \) in each step of \( m \). Starting time point of the pulse sequence \( t^0 \) is for excitation period not relevant and can be set to zero.
Figure 2.21: Spin counting MQ experiment under MAS. Reconstruction period follows immediately excitation period and both are rotor synchronized. R.f. pulses acting during excitation period are shifted as follows: \( \phi = m \cdot \Delta \phi \), where \( m = 0, 1, \ldots, q - 1 \) (more details see text). Undesired coherences are dephased during purging period \( n_0 \tau_r \) \((n_0 = 1, 2, \ldots)\).

During reconversion period higher order coherences are reconverted to longitudinal magnetization. In spin counting experiment reconversion period follows immediately excitation period resulting in the initial phase to be the same like for the excitation Hamiltonian \((t^0 = n \cdot \tau_r \equiv t^0 = 0)\). This can be simply written as:

\[
\hat{H}_{\text{rec}}^{\text{DQ}} = -\sum_{i<j} \left\{ \omega_{ij}(\theta, \psi, t^0 = 0) \hat{T}_{2,2}^{ij} + \omega_{ij}^*(\theta, \psi, t^0 = 0) \hat{T}_{2,-2}^{ij} \right\}.
\] (2.54)

Minus sign presented in above equation takes care for the time reversibility of the reconstruction Hamiltonian.

Calculating of the intensity of the signal resulting from two successive periods excitation and reconversion it will be found that it arise in longitudinal magnetization (see also appendix C). DQ part of that signal is modulated by the \( \cos(2 \Delta \phi \cdot m) \) (see section 3.2) term. Presence of the cosine factor shows that negative and positive frequencies can not be distinguished corresponding to the single-channel detection ([SR94]). Fourier transformation according to \( m \) will shift DQ signal by the frequency \( 2 \Delta \phi \cdot f_{sw} \), where \( f_{sw} \) is the half spectral width. In general each \( p \)-quantum order will be shifted by \( p \Delta \phi \cdot f_{sw} \). Because effective average Hamiltonian representing by equations (2.53) and (2.54) is a "pure" DQ one ([War80]) it can excite only even orders of coherence. Therefore, visible coherences will be \( p = 0, 2, 4, 6, \ldots, \leq p_{\text{max}} \).

It is important to note that the \( p \)-quantum signal consequent upon spin counting experiment is strictly periodic with the period \( 2\pi \). Hence it is enough to vary the phase

\(^{11}\)Reconversion Hamiltonian is rotor modulated (see e.g. equations (2.43)) and thus any changes in the phase by \( 2\pi \) are not relevant.
\( \phi \) only in the range \( 0 \ldots 2\pi \). Number of phase increments \( q \) can not be varied arbitrary \( (m = 0, 1, \ldots, q - 1) \). Only complete phase cycles can be sampled and thus \( q \) has to fulfil condition \( q = k \cdot 2p_{max} \), where \( k (k = 1, 2, \ldots) \) represent periodicity. In addition numerical Fourier transformation (\textit{fast fourier transform}, FFT) requires \( 2^j \) \((j \in \mathbb{N})\) data sets and thus \( k \cdot p_{max} = 2^j \) for obtaining correct results. Experimental results on Adamantane will be presented in section 3.4.