

Appendix

A. Irreducible tensors

Basic relations:

$$\begin{aligned}\hat{\mathbf{I}}_{\pm}^i &= \hat{\mathbf{I}}_x^i \pm i\hat{\mathbf{I}}_y^i \\ \hat{\mathbf{I}}_x^i &= \frac{1}{2}(\hat{\mathbf{I}}_+^i + \hat{\mathbf{I}}_-^i) \\ \hat{\mathbf{I}}_y^i &= \frac{i}{2}(\hat{\mathbf{I}}_-^i - \hat{\mathbf{I}}_+^i) .\end{aligned}\tag{A.1}$$

Single spin irreducible operators:

$$\begin{aligned}\hat{\mathbf{T}}_{1,0}^i &= \hat{\mathbf{I}}_z^i \\ \hat{\mathbf{T}}_{1,\pm 1}^i &= \mp \frac{1}{\sqrt{2}}(\hat{\mathbf{I}}_x^i \pm i\hat{\mathbf{I}}_y^i) .\end{aligned}\tag{A.2}$$

Irreducible tensors for two spin system coupled via dipolar coupling:

$$\begin{aligned}\hat{\mathbf{T}}_{2,0}^{ij} &= \frac{1}{\sqrt{6}}(3\hat{\mathbf{I}}_z^i\hat{\mathbf{I}}_z^j - \vec{\mathbf{I}}^i \cdot \vec{\mathbf{I}}^j) \\ \hat{\mathbf{T}}_{2,\pm 1}^{ij} &= \mp \frac{1}{2}(\hat{\mathbf{I}}_z^i\hat{\mathbf{I}}_{\pm}^j + \hat{\mathbf{I}}_{\pm}^i\hat{\mathbf{I}}_z^j) \\ \hat{\mathbf{T}}_{2,\pm 2}^{ij} &= \frac{1}{2}\hat{\mathbf{I}}_{\pm}^i\hat{\mathbf{I}}_{\pm}^j .\end{aligned}\tag{A.3}$$

We can drop indexes in equation (A.3) and for two spins I^i and I^j we will write ($\alpha = x, y, z$ and $k = 0, 1, 2$):

$$\begin{aligned}\hat{\mathbf{I}}_{\alpha} &= \hat{\mathbf{I}}_{\alpha}^i + \hat{\mathbf{I}}_{\alpha}^j \\ \hat{\mathbf{T}}_{2,k} &= 2\hat{\mathbf{T}}_{2,k}^{ij} .\end{aligned}\tag{A.4}$$

With the help of these definitions the relations in Tables A.1 and A.2 can be derived.

Table A.1: *Effect of dipolar Hamiltonian $\hat{H}_D = -\sqrt{\frac{2}{3}}\omega_D \hat{T}_{2,0}$ on spherical tensor operators.*

$\hat{\rho}$	$e^{i\sqrt{\frac{2}{3}}\hat{T}_{2,0}\omega_D t} \hat{\rho} e^{-i\sqrt{\frac{2}{3}}\hat{T}_{2,0}\omega_D t}$	
\hat{I}_z	\hat{I}_z	(invariant)
$\hat{T}_{2,0}$	$\hat{T}_{2,0}$	(invariant)
$(\hat{T}_{2,2} \pm \hat{T}_{2,-2})$	$(\hat{T}_{2,2} \pm \hat{T}_{2,-2})$	(invariant)
\hat{I}_x	$\hat{I}_x \cos(\omega_D t) - i(\hat{T}_{2,1} + \hat{T}_{2,-1}) \sin(\omega_D t)$	
\hat{I}_y	$\hat{I}_y \cos(\omega_D t) - (\hat{T}_{2,1} - \hat{T}_{2,-1}) \sin(\omega_D t)$	
$(\hat{T}_{2,1} + \hat{T}_{2,-1})$	$(\hat{T}_{2,1} + \hat{T}_{2,-1}) \cos \omega_D t - i\hat{I}_x \sin(\omega_D t)$	
$(\hat{T}_{2,1} - \hat{T}_{2,-1})$	$(\hat{T}_{2,1} - \hat{T}_{2,-1}) \cos \omega_D t + \hat{I}_y \sin(\omega_D t)$	

Table A.2: *Effect of 90° r.f. pulses x, y on spherical tensor operators, respectively.*

$\hat{\rho}$	$e^{\mp i\frac{\pi}{2}\hat{I}_x} \hat{\rho} e^{\pm i\frac{\pi}{2}\hat{I}_x}$	$e^{\mp i\frac{\pi}{2}\hat{I}_y} \hat{\rho} e^{\pm i\frac{\pi}{2}\hat{I}_y}$
\hat{I}_z	$\mp \hat{I}_y$	$\pm \hat{I}_x$
\hat{I}_x	\hat{I}_x (invariant)	$\mp \hat{I}_z$
\hat{I}_y	$\pm \hat{I}_z$	\hat{I}_y (invariant)
$\hat{T}_{2,0}$	$-\frac{1}{2}\hat{T}_{2,0} - \sqrt{\frac{3}{8}}(\hat{T}_{2,2} + \hat{T}_{2,-2})$	$-\frac{1}{2}\hat{T}_{2,0} + \sqrt{\frac{3}{8}}(\hat{T}_{2,2} + \hat{T}_{2,-2})$
$(\hat{T}_{2,1} + \hat{T}_{2,-1})$	$-(\hat{T}_{2,1} + \hat{T}_{2,-1})$	$\mp(\hat{T}_{2,2} - \hat{T}_{2,-2})$
$(\hat{T}_{2,1} - \hat{T}_{2,-1})$	$\mp i(\hat{T}_{2,2} - \hat{T}_{2,-2})$	$-(\hat{T}_{2,1} - \hat{T}_{2,-1})$
$(\hat{T}_{2,2} + \hat{T}_{2,-2})$	$-\sqrt{\frac{3}{2}}\hat{T}_{2,0} + \frac{1}{2}(\hat{T}_{2,2} + \hat{T}_{2,-2})$	$\sqrt{\frac{3}{2}}\hat{T}_{2,0} + \frac{1}{2}(\hat{T}_{2,2} + \hat{T}_{2,-2})$
$(\hat{T}_{2,2} - \hat{T}_{2,-2})$	$\mp i(\hat{T}_{2,1} - \hat{T}_{2,-1})$	$\pm(\hat{T}_{2,1} + \hat{T}_{2,-1})$

B. Wigner rotation matrices

The coordinate transformation with Euler angles $(\varphi, \vartheta, \psi)$ is described by the Wigner rotation matrices $\mathcal{D}_{k,q}^{(L)}$ given by ([SR94, Hae76])

$$\mathcal{D}_{k,q}^{(L)}(\varphi, \vartheta, \psi) = e^{-ik\varphi} d_{k,q}^{(L)}(\vartheta) e^{-iq\psi}, \quad (\text{B.1})$$

where factors $d_{k,q}^{(2)}(\vartheta)$ relevant for this work are defined in Table B.1.

A useful relation of the Wigner matrices is their 'addition theorem'. It relates the Wigner matrices of two successive rotations $A \rightarrow B$ and $B \rightarrow C$ to the Wigner matrices of overall rotation $A \rightarrow C$:

$$\mathcal{D}_{q,q'}^{(L)}(\Omega_{AC}) = \sum_{m=-L}^L \mathcal{D}_{q,m}^{(L)}(\Omega_{AB}) \mathcal{D}_{m,q'}^{(L)}(\Omega_{BC}). \quad (\text{B.2})$$

Euler angle $\Omega_{AC} = (\varphi_{AC}, \vartheta_{AC}, \psi_{AC})$ represents overall rotation $A \rightarrow C$, etc.

Table B.1: ϑ dependent factors $d_{k,q}^{(2)}(\vartheta)$ of the Wigner functions $\mathcal{D}_{k,q}^{(L)}(\varphi, \vartheta, \psi)$.

$d_{k,q}^{(2)}(\vartheta)$	$q = 2$	$q = 1$	$q = 0$
$k = 2$	$\frac{1}{4}(1 + \cos \vartheta)^2$	$-\frac{1}{2}(1 + \cos \vartheta) \sin \vartheta$	$\sqrt{\frac{3}{8}} \sin^2 \vartheta$
$k = 1$	$\frac{1}{2}(1 + \cos \vartheta) \sin \vartheta$	$\frac{1}{2}(\cos \vartheta - 1) + \cos^2 \vartheta$	$-\sqrt{\frac{3}{8}} \sin 2\vartheta$
$k = 0$	$\sqrt{\frac{3}{8}} \sin^2 \vartheta$	$\sqrt{\frac{3}{8}} \sin 2\vartheta$	$\frac{1}{2}(3 \cos^2 \vartheta - 1)$
$k = -1$	$\frac{1}{2}(1 - \cos \vartheta) \sin \vartheta$	$\frac{1}{2}(1 + \cos \vartheta) - \cos^2 \vartheta$	$\sqrt{\frac{3}{8}} \sin 2\vartheta$
$k = -2$	$\frac{1}{4}(1 - \cos \vartheta)^2$	$\frac{1}{2}(1 - \cos \vartheta) \sin \vartheta$	$\sqrt{\frac{3}{8}} \sin^2 \vartheta$
$d_{k,q}^{(2)}(\vartheta)$	$q = -1$	$q = -2$	
$k = 2$	$-\frac{1}{2}(1 - \cos \vartheta) \sin \vartheta$	$\frac{1}{4}(1 - \cos \vartheta)^2$	
$k = 1$	$\frac{1}{2}(1 + \cos \vartheta) - \cos^2 \vartheta$	$-\frac{1}{2}(1 - \cos \vartheta) \sin \vartheta$	
$k = 0$	$-\sqrt{\frac{3}{8}} \sin 2\vartheta$	$\sqrt{\frac{3}{8}} \sin^2 \vartheta$	
$k = -1$	$\frac{1}{2}(\cos \vartheta - 1) + \cos^2 \vartheta$	$-\frac{1}{2}(1 + \cos \vartheta) \sin \vartheta$	
$k = -2$	$\frac{1}{2}(1 + \cos \vartheta) \sin \vartheta$	$\frac{1}{4}(1 + \cos \vartheta)^2$	

C. Intensity of the DQ coherence for two spins- $\frac{1}{2}$ coupled via dipolar coupling

Intensity of the signal S_I just after the reconversion period in MQ experiment is going to be calculated. System of two spins- $\frac{1}{2}$ coupled via dipolar coupling isolated from the surrounding will be only considered. It will be shown that DQ signal just after the reconversion period is stored in the longitudinal magnetization. Considering this assumption no evolution during purging period between reconversion and detection pulse (see e.g. Figure 2.20) take place because of the vanishing commutator relation $[\hat{T}_{2,0}, \hat{I}_z] = 0$ valid for dipolar coupled spins (see also equation (1.59)). Under this circumstance DQ signal just after the reconversion period is assumed to be the signal detected just after the detecting pulse.

In addition if so-called total spin coherence ([Wei83, Mun87]) is excited during excitation period all coupled spins are active in MQ coherences, therefore, no evolution (during evolution period) under total dipolar Hamiltonian (equation (1.59)) take place. Assuming this condition signal intensity just after the reconversion period can be written as

$$S_I = \frac{\text{Tr} \left\{ \hat{I}_z \hat{U}_{rec} \hat{U}_{exc} c \hat{I}_z \hat{U}_{exc}^+ \hat{U}_{rec}^+ \right\}}{\text{Tr} \left\{ \hat{I}_z c \hat{I}_z \right\}}. \quad (\text{C.1})$$

\hat{U}_{exc} and \hat{U}_{rec} are propagators for excitation and reconversion period, respectively. Initial state of the system is $\hat{\rho}(0) = c \hat{I}_z$. Invariance of the trace from the cyclic change of the operators can be used for equation (C.1) and we will get $(\text{Tr} \{ \hat{I}_z^2 \} = 2$ for two spin- $\frac{1}{2}$ system)

$$S_I = \frac{1}{2} \text{Tr} \left\{ \hat{U}_{rec}^+ \hat{I}_z \hat{U}_{rec} \hat{U}_{exc} \hat{I}_z \hat{U}_{exc}^+ \right\}. \quad (\text{C.2})$$

We will for the moment assume that $\hat{U}_{rec} = \hat{U}_{exc}^+ = e^{i\hat{H}_{DQ}t}$. This is good valid for static solids. In general it is also valid for rotating solids with an exception that reconversion Hamiltonian is in addition rotor modulated (see e.g. equations (2.52) and (2.48)). To calculate equation (C.2) it is enough to concentrate to the evaluation of the term

$$f(t) \stackrel{\text{def}}{=} \hat{U} \hat{I}_z \hat{U}^+, \quad (\text{C.3})$$

where \hat{U} will be expressed in the form $\hat{U} = e^{-i\hat{H}_{DQ}t}$. At this point it is good to define DQ Hamiltonian in the general form $\hat{H}_{DQ} = \sum_{i < j} \omega_{ij} \hat{T}_{2,2}^{ij} + \omega_{ij}^* \hat{T}_{2,-2}^{ij}$ which represents time independent average Hamiltonian during excitation period as well as during reconversion

period for particular pulse sequence (see e.g sections 2.5.1.1 - 2.5.1.3 or section 2.4.1.2). Propagator of the time independent average Hamiltonian is than given as

$$\hat{U} = e^{-i \sum_{i < j} (\omega_{ij} \hat{T}_{2,2}^{ij} + \omega_{ij}^* \hat{T}_{2,-2}^{ij}) t}. \quad (C.4)$$

In general operators in exponent do not commute and thus we will now assume only two spin approximation. Hence, in the limit of two spin system interaction summation from equation (C.4) can be removed. Substituting propagator \hat{U} in equation (C.3) with above equation we will get

$$f(t) = e^{-i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} \hat{I}_z e^{i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t}. \quad (C.5)$$

Differentiating of this equation by time up to the second order and using commutator relation valid for two spin- $\frac{1}{2}$ system

$$[\hat{T}_{2,\pm 2}^{ij}, \hat{I}_z] = \mp 2 \hat{T}_{2,\pm 2}^{ij}, \quad (C.6)$$

we will get

$$\begin{aligned} \dot{f}(t) &= -i e^{-i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} [\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}, \hat{I}_z] e^{i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} \\ &= 2i e^{-i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} (\omega \hat{T}_{2,2}^{ij} - \omega^* \hat{T}_{2,-2}^{ij}) e^{i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} \end{aligned} \quad (C.7)$$

$$\begin{aligned} \ddot{f}(t) &= 2 e^{-i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} [\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}, \omega \hat{T}_{2,2}^{ij} - \omega^* \hat{T}_{2,-2}^{ij}] e^{i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} \\ &= -4 (\omega \cdot \omega^*) e^{-i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} [\hat{T}_{2,2}^{ij}, \hat{T}_{2,-2}^{ij}] e^{i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t}. \end{aligned} \quad (C.8)$$

In the limit of two spin interaction we can write commutator in equation (C.8) as

$$[\hat{T}_{2,2}^{ij}, \hat{T}_{2,-2}^{ij}] = \frac{1}{4} (\hat{I}_z^i + \hat{I}_z^j) = \frac{1}{4} \hat{I}_z, \quad (C.9)$$

so second derivation of the $f(t)$ can be now directly evaluated

$$\ddot{f}(t) = -|\omega|^2 e^{-i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} \hat{I}_z e^{i(\omega \hat{T}_{2,2}^{ij} + \omega^* \hat{T}_{2,-2}^{ij}) t} = -|\omega|^2 f(t). \quad (C.10)$$

This represents differential equation with the formal solution

$$f(t) = A \cos(|\omega|t) + B \sin(|\omega|t). \quad (C.11)$$

Arguments A and B can be simply derived comparing results from equations (C.5), (C.7) at $t = 0$ ($f(t=0)$, $\dot{f}(t=0)$). It can be found that

$$A = \hat{I}_z \quad \text{and} \quad B = 2i \left(\frac{\omega}{|\omega|} \hat{T}_{2,2}^{ij} - \frac{\omega^*}{|\omega|} \hat{T}_{2,-2}^{ij} \right). \quad (C.12)$$

If $f(t)$ is already known intensity of the signal S_I at the end of the reconversion period can be calculated (see equation (C.2)). Under the assumption $\hat{U}_{rec} = \hat{U}_{exc}^+$ and relations valid for two spin- $\frac{1}{2}$ system

$$\hat{T}_{2,\pm 2}^{ij} \cdot \hat{T}_{2,\pm 2}^{ij} = 0 \quad \text{and} \quad \text{Tr} \left\{ \hat{T}_{2,\pm 2}^{ij} \cdot \hat{I}_z \right\} = 0 \quad (\text{C.13})$$

the signal intensity gets the form

$$S_I = \frac{1}{2} \text{Tr} \left\{ f(t)^2 \right\} = \frac{1}{2} \text{Tr} \left\{ \hat{I}_z^2 \cos^2(|\omega|t) \right\} + \text{Tr} \left\{ 2 \left(\hat{T}_{2,2}^{ij} \cdot \hat{T}_{2,-2}^{ij} + \hat{T}_{2,-2}^{ij} \cdot \hat{T}_{2,2}^{ij} \right) \sin^2(|\omega|t) \right\}. \quad (\text{C.14})$$

The second term in this equation correspond to the DQ signal and the first one represents the polarization of the spin system and has to be filtered out from the spectrum. The first term also can not be manipulated through e.g. TPPI (see section 2.4.3) and will appear at the different frequency position as DQ coherence. Using the condition valid for two spin- $\frac{1}{2}$ system

$$\text{Tr} \left\{ \hat{T}_{2,2}^{ij} \cdot \hat{T}_{2,-2}^{ij} + \hat{T}_{2,-2}^{ij} \cdot \hat{T}_{2,2}^{ij} \right\} = \text{Tr} \left\{ \frac{1}{8} \hat{\mathbf{1}} \right\} = \frac{1}{2} \quad (\text{C.15})$$

intensity of DQ coherence from equation (C.14) can be simply evaluated

$$S_I^{DQ} = \sin^2(|\omega|t). \quad (\text{C.16})$$

The rest magnetization of the spin system is than

$$M_z = \cos^2(|\omega|t). \quad (\text{C.17})$$

In the case when $\hat{U}_{rec} \neq \hat{U}_{exc}^+$ the result given in equation for DQ intensity is not more valid and equation (C.2) has to be solved in more details. One has to calculate separately differential equation for reconversion period and the result will end up with the following equation¹

$$S_I^{DQ} = \Phi_\omega \sin(|\omega_{rec}|t) \sin(|\omega_{exc}|t), \quad (\text{C.18})$$

where

$$\Phi_\omega = \frac{\omega_{rec} \omega_{exc}^* + \omega_{rec}^* \omega_{exc}}{2 |\omega_{rec}| |\omega_{exc}|}. \quad (\text{C.19})$$

Complex terms ω_{exc} and ω_{rec} represent amplitudes and phases of DQ excitation and reconversion Hamiltonian one by one. Φ_ω is the phase of the DQ signal. t is excitation/reconversion time usually marked in this work like τ . To write equations (C.18) and (C.19) in more convenient way it is useful to separate amplitude and the phase from ω so:

¹We will assume that duration of the excitation and the reconversion period is equal $t_{exc} = t_{rec} = t$.

$\omega_{rec} = |\omega_{rec}|e^{i\Phi_{rec}}$, $\omega_{exc} = |\omega_{exc}|e^{i\Phi_{exc}}$. Using this definitions equations (C.18) and (C.19) will become more transparent. It holds that

$$S_I^{DQ} = \cos(\Phi_{rec} - \Phi_{exc}) \sin(|\omega_{rec}|\tau) \sin(|\omega_{exc}|\tau). \quad (\text{C.20})$$

The phase modulation of the DQ signal is from above equation evident from cosine factor $\cos(\Phi_{rec} - \Phi_{exc})$. It has to be noted that this phase modulation has no influence to the signal originating from the polarization of the spin system described by equation (C.17).