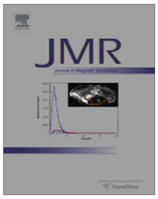
Journal of Magnetic Resonance 212 (2011) 11–16

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr



# A scaling factor theorem for homonuclear dipolar decoupling in solid-state NMR spectroscopy

Elodie Salager [a], Jean-Nicolas Dumez [a], Lyndon Emsley [a,*], Malcolm H. Levitt [b]

[a] Université de Lyon, CNRS/ENS-Lyon/UCB-Lyon 1, Centre de RMN à très hauts champs, 5 rue de la Doua, 69100 Villeurbanne, France
[b] Department of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

ARTICLE INFO

*Article history:*
Received 26 April 2011
Available online 12 June 2011

*Keywords:*
Solid-state NMR
Homonuclear dipolar decoupling
Average Hamiltonian Theory

ABSTRACT

A relationship between the dipolar and the chemical-shift scaling factors of cyclic radio-frequency irradiation schemes is introduced. This scaling factor theorem is derived analytically using Average Hamiltonian Theory, and its validity is illustrated numerically with homonuclear dipolar decoupling sequences generated randomly, and with the analysis of existing sequences. While derived for a static sample, the theorem provides insight into homonuclear dipolar decoupling schemes that combine radio-frequency irradiation with fast rotation of the sample at the magic-angle with respect to the static magnetic field.

## 1. Introduction

Hydrogen is the most abundant element in the universe, and its ubiquity makes it a potentially powerful probe for a large range of systems. Because of its high natural abundance and high magnetogyric ratio, which lead to a large equilibrium polarisation, the hydrogen nucleus should be the nucleus of choice for solid-state NMR spectroscopy, as it is in practice in solution-state NMR. In the solid state, however, the very same properties of protons also lead to the existence of strong internuclear couplings, which make it difficult to obtain high-resolution $^1$H NMR spectra.

Various radio-frequency (rf) irradiation schemes have been developed to remove the effect of homonuclear dipolar interactions in the NMR spectroscopy of solid samples. Such pulse sequences were initially developed with the aim of achieving, in either a step-wise [1] or a continuous manner [2], a rotation analogous to that achieved by mechanically spinning the sample at the magic-angle [3,4]. These original schemes have later been refined to achieve improved line-narrowing [5–17].

Radio-frequency homonuclear dipolar decoupling is, however, a double edged device. In the case of non-rotating samples, it cannot achieve any reduction of the effective magnitude of the dipolar interaction without also reducing the effective chemical shift interaction. More precisely, any rf irradiation scheme yields an apparent precession frequency for the nuclei which is smaller than their intrinsic precession frequency by a so-called chemical-shift scaling factor $\lambda$. This process collapses the chemical information of interest into a reduced spectral width, and the net effect of decoupling sequences is thus a subtle interplay between the narrowing of the peaks and the reduction of their separation in frequency space. These considerations are well known, and have been studied experimentally; it is in particular generally acknowledged that a pulse sequence that achieves perfect decoupling for a static sample cannot have a chemical-shift scaling factor larger than $1/\sqrt{3}$ [1,9,18,19]. However, no quantitative and rigorously derived statements, have been made on this subject.

Here we introduce a scaling factor theorem for homonuclear dipolar decoupling in solid-state NMR spectroscopy. The theorem consists in a relationship between the dipolar scaling factor and the chemical-shift scaling factor, valid for any cyclic rf-irradiation scheme applied to a static solid. We give a derivation of the theorem based on Average Hamiltonian Theory, and we illustrate its validity with numerical calculations of effective Hamiltonians for randomly generated pulse sequences. We also discuss the consequences of the theorem for the design of homonuclear dipolar decoupling schemes that combine pulsed rf-irradiation with rotation at the magic-angle.

## 2. The scaling factor theorem

In this section, the dipolar and chemical-shift scaling factors are first defined, and the scaling factor theorem is then stated. An analytical derivation based on Average Hamiltonian Theory is given in Section 3, and numerical simulations with randomly generated pulse sequences are described and discussed in Section 4.

### 2.1. Chemical-shift and dipolar scaling factors

In the limit of high magnetic field and for a system of homonuclear spins $I = 1/2$ coupled by the dipolar interaction, the internal rotating-frame secular Hamiltonian $H_S$ is

---

* Corresponding author. Fax: +33 478 896 761.
*E-mail address:* lyndon.emsley@ens-lyon.fr (L. Emsley).

1090-7807/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jmr.2011.05.017

$$H_S = \sum_i \left( \omega^i_{CS} T^i_{10} + \sum_{j>i} \omega^{ij}_D T^{ij}_{20} \right), \tag{1}$$

where the sums are over all spins *i* and *j* in the system, the first term is the chemical shift Hamiltonian $H_{CS}$ for spin *i*, with an offset $\omega^i_{CS}$ with respect to the rf irradiation frequency, and the second term is the dipolar Hamiltonian $H_D$ with $\omega^{ij}_D$ the dipolar coupling between spins *i* and *j*. Irreducible spherical tensors are used to express spin Hamiltonians, and their relationship to Cartesian operators are recalled in Table 1. Here we consider systems of protons, which in the solid state form strongly dipolar-coupled networks.

To act on the spin Hamiltonian, a time-dependent radio-frequency field is applied to the sample. The total spin Hamiltonian is therefore:

$$H(t) = H_S + H_{RF}(t). \tag{2}$$

For a radio-frequency interaction that is both periodic and cyclic, the time evolution of the system over one cycle of radio-frequency irradiation can be described by an effective Hamiltonian $\widetilde{H}$ or average Hamiltonian $\overline{H}$, the detailed properties and conditions of existence of which will be discussed below. $\widetilde{H}$ takes the general form:

$$\widetilde{H} = \sum_i \left( \omega^i_{CS} \sum_{\mu=-1}^{1} T^i_{1\mu} \lambda^{CS}_{1\mu} + \sum_{j>i} \omega^{ij}_D \sum\nolimits_{\mu=-2}^{2} T^{ij}_{2\mu} \lambda^D_{2\mu} \right). \tag{3}$$

The chemical-shift scaling factor $\lambda^{CS}$ is defined as the ratio between the norm of the linear Hamiltonian under radio-frequency irradiation and without radio-frequency irradiation,

$$\lambda^{CS} = \sqrt{\sum\nolimits_{\mu=-1}^{1} \left| \lambda^{CS}_{1\mu} \right|^2}. \tag{4}$$

The dipolar scaling factor $\lambda^D$ is defined in the same way for the second-rank part of the Hamiltonian,

$$\lambda^D = \sqrt{\sum\nolimits_{\mu=-2}^{2} \left| \lambda^D_{2\mu} \right|^2}. \tag{5}$$

In the context of homonuclear dipolar decoupling, the dipolar scaling factor characterises the magnitude of the residual dipolar interactions; the smaller the dipolar scaling factor, the better the line-narrowing efficiency of the decoupling sequence. As homonuclear dipolar decoupling aims at minimising $\lambda^D$ while maximising $\lambda^{CS}$, any relationship between the two imposes constraints on the development of decoupling sequences.

### 2.2. Theorem

For a static system of homonuclear spins $I = 1/2$ coupled by the dipolar interaction and submitted to a cyclic radio-frequency irradiation, the chemical-shift and dipolar scaling factors satisfy

$$\left| \lambda^{CS} \right|^2 \leqslant \frac{1}{3} \left( 2 \left| \lambda^D \right| + 1 \right). \tag{6}$$

The theorem states that the maximum value allowed for the chemical-shift scaling factor depends on the dipolar scaling factor. The allowed values of the dipolar and chemical-shift scaling factors can be represented graphically as in Fig. 1, which shows the limit imposed on rf-decoupling sequences. In particular, perfect decoupling, which corresponds to $\lambda^D = 0$, is a special case of Eq. (6) and yields the 'quasi-static' maximum of the chemical-shift scaling factor of $1/\sqrt{3}$.

**Table 1**
Relationship between the irreducible spherical components and the Cartesian components of rank-one and rank-two spin operators.

| Cartesian representation | Spherical components |
|---|---|
| $I=(I_x, I_y, I_z)$ | $T_{10} = I_z$<br>$T_{1\pm1} = \mp\frac{1}{\sqrt{2}}(I_x \pm iI_y) = \mp\frac{1}{\sqrt{2}} I_\pm$ |
| $T = \begin{pmatrix} I_xS_x & I_xS_y & I_xS_z \\ I_yS_x & I_yS_y & I_yS_z \\ I_zS_x & I_zS_y & I_zS_z \end{pmatrix}$ | $T_{20} = \frac{1}{\sqrt{6}}\left(3I_zS_z - \vec{I}\cdot\vec{S}\right)$<br>$T_{2\pm1} = \mp\frac{1}{2}(I_zS_\pm + I_\pm S_z)$<br>$T_{2\pm2} = \frac{1}{2} I_\pm S_\pm$<br>$T_{10} = -\frac{1}{2\sqrt{2}}(I_+S_- - I_-S_+)$<br>$T_{1\pm1} = \frac{1}{2}(I_zS_\pm - I_\pm S_z)$<br>$T_{00} = -\frac{1}{\sqrt{3}}(I_zS_z + I_xS_x + I_yS_y)$ |

## 3. Analytical derivation of the theorem

### 3.1. Average Hamiltonian

The following derivation relies on average Hamiltonian theory [20], and will be conducted in the interaction frame of the applied rf field. The radio-frequency propagator $U_{RF}(t)$ is defined as

$$\frac{d}{dt}(U_{RF}(t)) = -iH_{RF}(t)U_{RF}(t). \tag{7}$$

The Hamiltonian of the system $H_s$, in the rf interaction frame, transforms to

$$H'(t) = U^{-1}_{RF}(t) H_S U_{RF}(t). \tag{8}$$

If the radio-frequency irradiation is cyclic with a cycle time $\tau_c$, such that $U_{RF}(n\tau_c) = 1, \forall n$, the rf interaction frame and the rotating frame coincide at times $n\tau_c$ [20], and the evolution of the system under stroboscopic observation (at times $n\tau_c$) will be correctly described in either of the two frames. An average Hamiltonian that describes the evolution over a cycle can then be defined; the first-order average Hamiltonian is:

$$\overline{H}^1(\tau_c) = \frac{1}{\tau_c} \int_0^{\tau_c} dt' \; U^{-1}_{RF}(t') H_S U_{RF}(t'). \tag{9}$$

In order to avoid cumbersome notation, in the following we consider the chemical shift for a single spin, *i*, and the coupling with one other spin, *j*. The reasoning can be extended to more spins, as will be shown in Section 3.4. When only these interactions are included, the first-order average Hamiltonian [20] becomes

$$\overline{H}^1(\tau_c) = \frac{1}{\tau_c} \int_0^{\tau_c} dt' U^{-1}_{RF}(t')(H_{CS} + H_D) U_{RF}(t'). \tag{10}$$

As the radio-frequency field induces a rotation of the spins, its propagator can be expressed as:

$$U_{RF}(t) = R(\Omega_{RF}(t)), \tag{11}$$

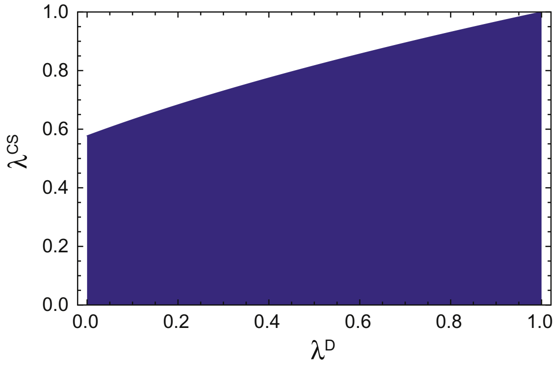


**Fig. 1.** The dark area shows the allowed values of the chemical-shift and dipolar scaling factors for cyclic rf irradiation applied to a static sample.

where $\Omega_{\mathrm{RF}}(t) = \{\alpha_{\mathrm{RF}}(t), \beta_{\mathrm{RF}}(t), \gamma_{\mathrm{RF}}(t)\}$ is the set of time-dependent Euler angles that define the rotation induced by the radio-frequency field: $R(\Omega_{\mathrm{RF}}(t)) = R_z(\alpha_{\mathrm{RF}}(t))R_y(\beta_{\mathrm{RF}}(t))R_z(\gamma_{\mathrm{RF}}(t))$.

As the rank of an operator is preserved by the rotation $R(\Omega_{\mathrm{RF}}(t))$, the first-order average Hamiltonian for the spin *i* under radio-frequency irradiation, as expressed in Eq. (10) can also be written as:

$$\overline{H}^1(\tau_c) = \omega_{\mathrm{CS}} \sum_{\mu=-1}^{1} T_{1\mu}\lambda_{1\mu}^{\mathrm{CS}} + \omega_{\mathrm{D}} \sum_{\mu=-2}^{2} T_{2\mu}\lambda_{2\mu}^{\mathrm{D}}, \tag{12}$$

where the terms $\lambda_{1\mu}^{\mathrm{CS}}$ are the components of the chemical-shift scaling factor and the terms $\lambda_{2\mu}^{\mathrm{D}}$ are the components of the dipolar scaling factor. In order to derive the relationship between the chemical-shift and the dipolar scaling factors, it is convenient to perform the additional transformation described in the following section.

### 3.2. Tilted average Hamiltonian

A rotation can be applied, that simplifies the expression of the average Hamiltonian for the spin *i*, such that the first-rank elements only have a component on $T_{10}$, as seen in Fig. 2,

$$\bar{H}^{1,T}(\tau_c) = \omega_{\mathrm{CS}}\lambda^{\mathrm{CS}}T_{10} + \omega_{\mathrm{D}} \sum_{\mu=-2}^{2} \lambda_{2\mu}^{\mathrm{D,T}}T_{2\mu}. \tag{13}$$

This corresponds to a rotation defined by a set of time-independent Euler angles, noted $\Omega_{\mathrm{T}}$ in the following discussion, and defined from the orientation of the average Hamiltonian at time $\tau_c$. The physical idea is to tilt the observation frame to a position such that the average Hamiltonian at time $\tau_c$ will only have a component on $T_{10}$.

We thus consider the combined rotation from the rotating frame to the tilted frame,

$$R(\Omega(t')) = R(\Omega_{\mathrm{RF}}(t'))R(\Omega_{\mathrm{T}}), \tag{14}$$

$\Omega(t) = \{\alpha(t), \beta(t), \gamma(t)\}$ describes the consecutive rotations under the radio-frequency interaction frame transformation and the transformation to the tilted Hamiltonian. The first-order tilted average Hamiltonian for spin *i*, using this overall rotation, is then expressed using Wigner rotation matrices [21]:

$$\begin{aligned}\overline{H}^{1,T}(\tau_c) &= \frac{1}{\tau_c}\int_0^{\tau_c} dt' R(\Omega(t'))^{-1}(\omega_{\mathrm{CS}}T_{10} + \omega_{\mathrm{D}}T_{20})R(\Omega(t')) \\ &= \omega_{\mathrm{CS}} \sum_{\mu=-1}^{1} T_{1\mu}\frac{1}{\tau_c}\int_0^{\tau_c} D_{\mu 0}^1\left(\Omega(t')^{-1}\right)dt' \\ &\quad + \omega_{\mathrm{D}} \sum_{\mu=-2}^{2} T_{2\mu}\frac{1}{\tau_c}\int_0^{\tau_c} D_{\mu 0}^2\left(\Omega(t')^{-1}\right)dt',\end{aligned} \tag{15}$$

where the terms $D_{m'm}^{l}(\Omega(t')^{-1})$ are the Wigner matrices associated with the Euler angles $\Omega(t')^{-1}$: $D_{m'm}^{l}(\Omega(t')^{-1}) = \exp(-im'\alpha)d_{\mu 0}^{l}(-\beta)\exp(-im\gamma)$

From the definition of the tilted average Hamiltonian (Eq. (13)), $\bar{H}^{1,\mathrm{T}}(\tau_c)$ only has a component on $T_{10}$. Therefore the integrals $\int_0^{\tau_c} D_{10}^1(\Omega(t')^{-1})dt'$ and $\int_0^{\tau_c} D_{-10}^1(\Omega(t')^{-1})dt'$ are zero, and the tilted average Hamiltonian is

$$\begin{aligned}\bar{H}^{1,T}(\tau_c) &= \omega_{\mathrm{CS}}T_{10}\frac{1}{\tau_c}\int_0^{\tau_c} D_{00}^1(\Omega(t')^{-1})dt' \\ &\quad + \omega_{\mathrm{D}} \sum_{\mu=-2}^{2} T_{2\mu}\frac{1}{\tau_c}\int_0^{\tau_c} D_{\mu 0}^2(\Omega(t')^{-1})dt' \\ &= \omega_{\mathrm{CS}}T_{10}\lambda^{\mathrm{CS}} + \omega_{\mathrm{D}} \sum_{\mu=-2}^{2} T_{2\mu}\lambda_{2\mu}^{\mathrm{D,T}}.\end{aligned} \tag{16}$$

### 3.3. Relationship between the chemical-shift and dipolar scaling factors

The aim is to determine the relationship between $\lambda^{\mathrm{CS}}$ and $\lambda^{\mathrm{D}}$. We consider in particular the relationship between $\lambda^{\mathrm{CS}}$ and $\lambda_{20}^{\mathrm{D,T}}$ in the tilted frame as a function of the Euler angle $\Omega(t) = \{\alpha(t), \beta(t), \gamma(t)\}$,

$$\begin{aligned}\lambda^{\mathrm{CS}} &= \frac{1}{\tau_c}\int_0^{\tau_c} D_{00}^1(\Omega(t')^{-1})dt' \\ &= \frac{1}{\tau_c}\int_0^{\tau_c} \exp(-i0\alpha(t))d_{00}^1(-\beta(t'))\exp(-i0\gamma(t))dt' \\ &= \frac{1}{\tau_c}\int_0^{\tau_c} \cos(\beta(t'))dt',\end{aligned} \tag{17}$$

$$\begin{aligned}\lambda_{20}^{\mathrm{D,T}} &= \frac{1}{\tau_c}\int_0^{\tau_c} D_{00}^2(\Omega(t')^{-1})dt' = \frac{1}{\tau_c}\int_0^{\tau_c} d_{00}^2(-\beta(t'))dt' \\ &= \frac{1}{\tau_c}\int_0^{\tau_c} \frac{1}{2}[3\cos^2(\beta(t')) - 1]dt'.\end{aligned}$$

Using the Cauchy–Schwarz inequality [22], the maximum value of the scaling factor can be determined,

$$\begin{aligned}\left|\frac{1}{\tau_c}\int_0^{\tau_c}(\cos(\beta(t'))\cdot 1)dt'\right|^2 &\leqslant \frac{1}{\tau_c}\int_0^{\tau_c}\cos^2(\beta(t'))dt'\cdot\frac{1}{\tau_c} \\ &\quad \times \int_0^{\tau_c} 1dt' \\ &\leqslant \frac{1}{3}\left(2|\lambda_{20}^{\mathrm{D,T}}| + 1\right),\end{aligned} \tag{18}$$

$$|\lambda^{\mathrm{CS}}|^2 \leqslant \frac{1}{3}\left(2|\lambda_{20}^{\mathrm{D,T}}| + 1\right). \tag{19}$$

The total dipolar scaling factor $\lambda^{\mathrm{D}}$ is defined as

$$|\lambda^{\mathrm{D}}|^2 = \sum_{\mu=-2}^{2}\left|\lambda_{2\mu}^{\mathrm{D,T}}\right|^2 > |\lambda_{20}^{\mathrm{D,T}}|^2. \tag{20}$$

Therefore, the relationship between the chemical-shift scaling factor and the total dipolar scaling factor can be written as

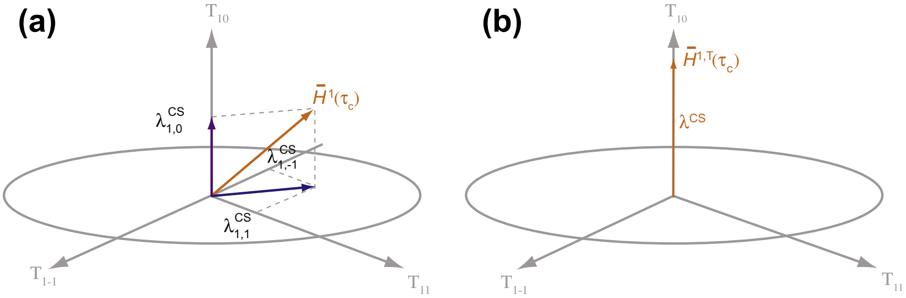


**Fig. 2.** Average Hamiltonian in the subspace of rank-one irreducible tensors. (a) The three components in the interaction frame. (b) The tilted Hamiltonian, where only the component on $T_{10}^{i}$ is non-zero.

$$|\lambda^{\mathrm{CS}}|^2 \leqslant \frac{1}{3}\left(2|\lambda^{\mathrm{D}}_{20}|+1\right) \leqslant \frac{1}{3}\left(2|\lambda_{\mathrm{D}}|+1\right). \tag{21}$$

which is the desired result.

### 3.4. Extension to more spins

When considering more than one dipolar coupling with the spin *i*, the average Hamiltonian becomes

$$\overline{H}^1(\tau_c) = \omega_{\mathrm{CS}} \sum_{\mu=-1}^{1} T_{1\mu}\lambda^{\mathrm{CS}}_{1\mu} + \sum_j \omega^j_{\mathrm{D}} \sum_{\mu=-2}^{2} T^{ij}_{2\mu}\lambda^{\mathrm{D},ij}_{2\mu}. \tag{22}$$

The Euler angle $\Omega_{\mathrm{T}}$ used to align the rank-one part of the average Hamiltonian with $T_{10}$ is independent of the dipolar couplings, as well as of the radio-frequency interaction frame transformation. Thus, the overall transformation $\Omega(t) = \{\alpha(t), \beta(t), \gamma(t)\}$ is the same for all the rank-two tensors. Consequently, the inequality is valid for each of the dipolar couplings to spin *i*:

$$|\lambda_{\mathrm{CS}}|^2 \leqslant \frac{1}{3}\left(2\left|\lambda^{\mathrm{D},ij}_{20}\right|+1\right) \leqslant \frac{1}{3}\left(2\left|\lambda^{\mathrm{D},ij}\right|+1\right), \qquad \forall j. \tag{23}$$

In this derivation, no assumption has been made about spin *i*. For a spin *k* with a different offset, the orientation of the average Hamiltonian in the radio-frequency interaction frame and consequently the overall rotation $\Omega^k(t) = \{\alpha^k(t), \beta^k(t), \gamma^k(t)\}$ is slightly different. The rank-one and rank-two scaling factors for spin k are, however, both expressed as a function of the angle $\beta^k(t)$, and thus also verify the scaling factor theorem.

## 4. Numerical verification of the theorem for randomly generated decoupling sequences

The scaling factor theorem can be illustrated by numerical studies of randomly generated pulse sequences. To complement the analytical derivation of the theorem, we have carried out numerical calculations of the chemical-shift and dipolar scaling factors for a static two-spin system.

### 4.1. The DUMBO framework

The modulation schemes used in the DUMBO framework [13] provide a convenient way to explore the propagator space spanned by rf-decoupling schemes, since the radio-frequency field has a constant amplitude $\omega_{\mathrm{RF}}$ and is phase modulated according to the coefficients of a Fourier series. Although not exhaustive, a search performed with sequences using randomly generated Fourier coefficients explores a large fraction of propagator space. It is important to note that the validity of the scaling factor theorem is not limited to pulse sequences that can be expressed within this framework.

In our calculations, the phase modulation is thus specified by a Fourier series over one decoupling cycle $\tau_c$:

$$\begin{cases} \varphi(t) = a_0 + \sum\limits_{n=1}^{6}\left(a_n \cos\left(n\frac{2\pi}{(\tau_c/2)}t\right) + b_n \sin\left(n\frac{2\pi}{(\tau_c/2)}t\right)\right), & 0 < t < \frac{\tau_c}{2} \\ \varphi(t) = \pi + \varphi(\tau_c - t), & \frac{\tau_c}{2} < t < \tau_c \end{cases}, \tag{24}$$

where $\tau_c$ is the duration of one cycle, chosen to be $\tau_c \approx 3T_{\mathrm{RF}} = 6\pi/\omega_{\mathrm{RF}}$. The second half of the phase modulation is fully determined from the first half by a π-shift and time reversal, in order to ensure that the radio-frequency Hamiltonian is cyclic and has time-reversal symmetry [20].

### 4.2. Calculation of effective Hamiltonians

For a system evolving under the time-dependent Hamiltonian H, the density matrix operator $\sigma(t)$ at time t is given by

$$\sigma(t) = U(t,0)\sigma(0)U^{-1}(t,0), \tag{25}$$

where

$$U(t,0) = T\exp\left(\int_0^t -iH(t')dt'\right), \tag{26}$$

and where $\sigma(0)$ is the initial density matrix. For a time-periodic Hamiltonian of period $\tau_c$, it is of interest to define an effective Hamiltonian, $H_{\mathrm{eff}}$, as

$$U(\tau_c, 0) = \exp(-iH_{\mathrm{eff}}\tau_c). \tag{27}$$

The effective Hamiltonian describes the evolution over one period of the time-dependent interaction; it can be calculated by taking the logarithm of the propagator $U(\tau_c,0)$, which can itself be obtained according to Eq. (26). Using the expression given in Eq. (2) for the Hamiltonian, the propagator over one cycle can be calculated numerically as:

$$U(\tau_c) = \prod_{j=1}^{N} \exp\left(-i[H_{\mathrm{CS}} + H_{\mathrm{D}} + H_{\mathrm{RF}}(j)]\Delta t\right), \tag{28}$$

where $\Delta t$ is the length of each of the *N* steps in the phase modulation and $H_{\mathrm{RF}}(j)$ is the value of the radio-frequency Hamiltonian for step *j* of the digitized phase modulation. The effective Hamiltonian is then derived numerically through diagonalisation of the effective propagator [23]. It should be noted that the step-by-step calculation of the propagator is particularly pertinent, since it corresponds to the step-wise manner used to implement the radio-frequency phase modulation on the spectrometer. This approach for the calculation of effective Hamiltonians was notably used for the development of the DUMBO-1 pulse sequence [13].

### 4.3. Chemical-shift and dipolar scaling factors

Once an effective Hamiltonian has been obtained, the dipolar and chemical-shift scaling factors can be calculated (both procedures are described in Supplementary Information). Fig. 3 shows the chemical-shift scaling factor plotted as a function of the dipolar scaling factor, for around 2 million sequences generated randomly within the DUMBO framework, i.e., according to Eq. (24) with random values for the Fourier coefficients $a_n$ and $b_n$. The theoretical maximum of the chemical-shift scaling factor as a function of the dipolar scaling factor, given by Eq. (23), is plotted as a solid red line. Again, it can be seen that a larger value of the chemical-shift scaling factor can only be accessed at the cost of a reduced line-narrowing efficiency. In particular, all sequences with a dipolar scaling factor less than 0.04 have a scaling factor less than the 'static' maximum of $1/\sqrt{3}$, as shown by the red dashed line.

The sequences actually developed for good homonuclear dipolar decoupling in static solids can be analysed in the context of the scaling factor theorem. The WAHUHA sequence and LG sequence and their subsequent refinements, which achieve a cubic symmetry in a step-wise or continuous manner, yield a dipolar scaling factor close to zero, and a chemical-shift scaling factor of $1/\sqrt{3}$ or less. The DUMBO-1 sequence [13], which was designed to have the smallest possible dipolar scaling factor in simulations performed with a static sample has a dipolar scaling factor of less than 0.03 and a chemical-shift scaling factor close to the maximum value of $1/\sqrt{3}$.

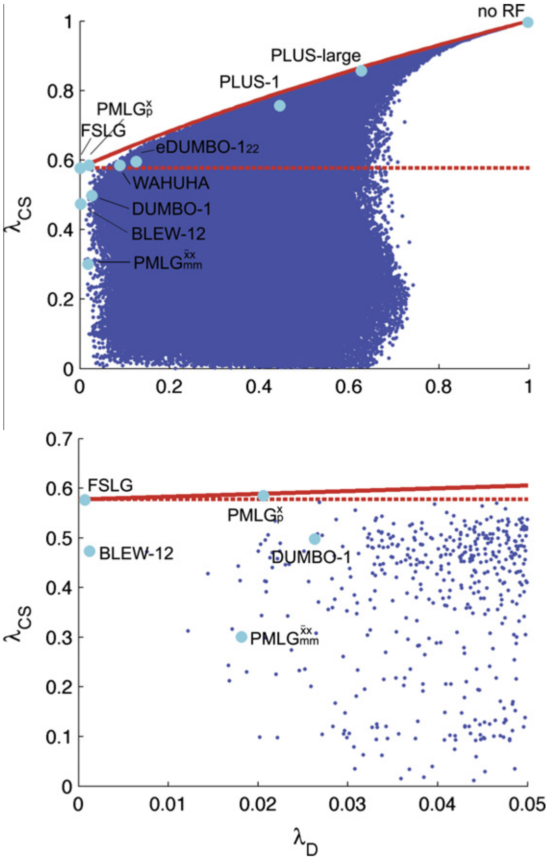


**Fig. 3.** (a) Calculated CS scaling factors as a function of the dipolar scaling factor for 2 million rf schemes defined using random Fourier coefficients, and for FSLG, PMLG$_p^x$, PMLG$_{mm}^{x\bar{x}}$, WAHUHA, BLEW-12, DUMBO-1, eDUMBO-1$_{22}$, PLUS-1, PLUS-large and no radio-frequency irradiation. (b) Expansion of (a), showing the region of the best dipolar scaling factor. The red line shows the theoretical maximum for the CS scaling factor. Scaling factors were calculated using a home-written MATLAB® (2008a, The MathWorks, Natick, MA) routine for two spins under static conditions, using a dipolar coupling $\omega_D/2\pi$ of 10 kHz (as defined in Eq. (1)), a radio-frequency field amplitude $\omega_{RF}/2\pi$ of 170 kHz and relative resonance offsets of 3.5 kHz. The other parameters were chosen to match the experimental implementation for each decoupling sequence. The DUMBO-1, eDUMBO-1$_{22}$, PLUS-1 and PLUS-large sequences were calculated for a cycle time $\tau_c$ of 20 μs, with the phase modulation being implemented experimentally using 200 steps of 100 ns. BLEW-12, PMLG$_p^x$ and PMLG$_{mm}^{x\bar{x}}$ were implemented with 12, 10 and 20 steps respectively and the delays between pulses for WAHUHA were 6 μs. FSLG was implemented with offsets of 121 and 124.5 kHz. All scripts are given in Supplementary Information.

## 5. Consequences for spinning solids

The theorem given here corresponds to the case of a static sample, for which the internal interactions are time-independent. For homonuclear dipolar decoupling, its validity can be extended to the so-called quasi-static regime, where the cycle duration of the rf pulse sequence is short compared to the sample rotation period. For experiments performed at higher spinning frequencies, MAS can significantly affect dipolar interactions. As first suggested by Spiess and coworkers [11,24,25], it then becomes possible to use pulse sequences that yield a non-zero dipolar scaling factor, and a chemical-shift scaling factor larger than $1/\sqrt{3}$, i.e., to explore the region of Fig. 3 located further away from the $\lambda_D = 0$ axis.

It can be seen in Fig. 3 that the eDUMBO-1$_{22}$ sequence [26], which was obtained through an experimental optimisation procedure performed at 22 kHz MAS, has a chemical-shift scaling factor of 0.59, and a slightly poorer dipolar scaling factor than DUMBO-1. *A posteriori*, eDUMBO-1$_{22}$ can be seen as a first exploration with DUMBO sequences of a wider propagator space, made possible by MAS. It still lies relatively close to the DUMBO-1 sequence, which operates in the quasi-static regime, as 22 kHz is only a moderate spinning frequency compared to the magnitude of typical proton-proton dipolar couplings, and because DUMBO-1 was used as a seed in the optimisation procedure.

Recently, decoupling sequences have been developed within the DUMBO framework which have large chemical-shift scaling factors [27]. These sequences, called PLUS-1 and PLUS-large, have a relatively poor intrinsic line-narrowing efficiency, but make full use of the effect of ultrafast magic-angle spinning on dipolar couplings. In Fig. 3, PLUS-1 and PLUS-large can be seen to lie very close to the maximum value of the chemical-shift scaling factor allowed for a given dipolar scaling factor. The scaling factor theorem thus makes it possible to illustrate quantitatively the fact that PLUS-1 works well outside the quasi-static regime, and the experimental optimisation procedure was efficient at finding an appropriate compromise between dipolar scaling factor and chemical-shift scaling factor for a given spinning frequency.

It can be noted that in the limit of infinitely fast spinning, perfect line-narrowing is achieved without any rf irradiation. This situation is indicated in Fig. 3 as the point $\lambda_D = \lambda_{CS} = 1$.

## 6. Conclusion

We have introduced and derived a relationship between the dipolar and the chemical-shift scaling factor of a cyclic rf pulse sequence. This scaling factor theorem imposes constraints on the development of homonuclear dipolar decoupling strategies, and we have illustrated these constraints with numerical calculations of dipolar and chemical-shift scaling factors for randomly generated pulse sequences, and with the analysis of existing decoupling sequences. The maximum value of the chemical-shift scaling factor for pulse sequences that achieves perfect decoupling for static solids is a special case of the theorem. For homonuclear dipolar decoupling under magic-angle spinning, the scaling factor theorem provides a criterion to identify and develop decoupling sequences that work outside the quasi-static regime.

## Acknowledgments

The authors thank Andrew J. Pell, Dimitris Sakellariou and Zhehong Gan for interesting discussions. This work was supported in part by a Grant from the Agence Nationale de la Recherche (ANR Blanc 06-1139312 – PSD-NMR).

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmr.2011.05.017.

## References

[1] J.S. Waugh, L.M. Huber, U. Haeberlen, Approach to high-resolution NMR in solids, Physical Review Letters 20 (1968) 180–182.
[2] M. Lee, W.I. Goldburg, Nuclear-magnetic-resonance line narrowing by a rotating rf field, Physical Review 140 (1965) A1261–A1271.
[3] E.R. Andrew, A. Bradbury, R.G. Eades, Nuclear magnetic resonance spectra from a crystal rotated at high speed, Nature 182 (1958) 1659.
[4] I.J. Lowe, Free induction decays of rotating solids, Physical Review Letters 2 (1959) 285–287.
[5] P. Mansfield, Symmetrized pulse sequences in high resolution NMR in solids, Journal of Physics C: Solid State Physics 4 (1971) 1444.
[6] W.K. Rhim, D.D. Elleman, R.W. Vaughan, Analysis of multiple pulse NMR in solids, Journal of Chemical Physics 59 (1973) 3740–3749.
[7] D.P. Burum, M. Linder, R.R. Ernst, Low-power multipulse line narrowing in solid-state NMR, Journal of Magnetic Resonance 44 (1969) 173–188 (1981).
[8] D.P. Burum, W.K. Rhim, Analysis of multiple pulse NMR in solids. 3, Journal of Chemical Physics 71 (1979) 944–956.

[9] A. Bielecki, A.C. Kolbert, M.H. Levitt, Frequency-switched pulse sequences: homonuclear decoupling and dilute spin NMR in solids, Chemical Physics Letters 155 (1989) 341–346.

[10] H. Liu, S.J. Glaser, G.P. Drobny, Development and optimization of multipulse propagators – applications to homonuclear spin decoupling in solids, Journal of Chemical Physics 93 (1990) 7543–7560.

[11] D.E. Demco, S. Hafner, H.W. Spiess, Rotation-synchronized homonuclear dipolar decoupling, Journal of Magnetic Resonance Series A 116 (1995) 36–45.

[12] M. Hohwy, N.C. Nielsen, Elimination of high order terms in multiple pulse nuclear magnetic resonance spectroscopy: application to homonuclear decoupling in solids, Journal of Chemical Physics 106 (1997) 7571–7586.

[13] D. Sakellariou, A. Lesage, P. Hodgkinson, L. Emsley, Homonuclear dipolar decoupling in solid-state NMR using continuous phase modulation, Chemical Physics Letters 319 (2000) 253–260.

[14] E. Vinogradov, P.K. Madhu, S. Vega, High-resolution proton solid-state NMR spectroscopy by phase-modulated Lee–Goldburg experiment, Chemical Physics Letters 314 (1999) 443–450.

[15] M. Leskes, P.K. Madhu, S. Vega, A broad-banded z-rotation windowed phase-modulated Lee–Goldburg pulse sequence for 1H spectroscopy in solid-state NMR, Chemical Physics Letters 477 (2008) 370.

[16] P.K. Madhu, X. Zhao, M.H. Levitt, High-resolution H-1 NMR in the solid state using symmetry-based pulse sequences, Chemical Physics Letters 346 (2001) 142–148.

[17] J.P. Amoureux, B. Hu, J. Trébosc, Enhanced resolution in proton solid-state NMR with very-fast MAS experiments, Journal of Magnetic Resonance 193 (2008) 305–307.

[18] L. Emsley, D.D. Laws, A. Pines, Lectures on pulsed NMR, in: B. Maraviglia (Ed.), Proceedings of the International School of Physics Enrico Fermi, third ed., Course CXXIX, IOS Press, Amsterdam, 1998.

[19] A. Lesage, D. Sakellariou, S. Hediger, B. Elena, P. Charmont, S. Steuernagel, L. Emsley, Experimental aspects of proton NMR spectroscopy in solids using phase-modulated homonuclear dipolar decoupling, Journal of Magnetic Resonance 163 (2003) 105–113.

[20] U. Haeberlen, J.S. Waugh (Eds.), High Resolution NMR in Solids: Selective Averaging, Academic Press, New York, 1976.

[21] A.A. Wolf, Rotation operators, American Journal of Physics 37 (1969) 531–536.

[22] G.B. Arfken, H.J. Weber, Mathematical Methods for Physicists, Elsevier Academic Press, London, 2005.

[23] M. Eden, Y.K. Lee, M.H. Levitt, Efficient simulation of periodic problems in NMR. Application to decoupling and rotational resonance, Journal of Magnetic Resonance Series A 120 (1996) 56–71.

[24] S. Hafner, H.W. Spiess, Multiple-pulse assisted line-narrowing by fast magic-angle spinning, Solid State Nuclear Magnetic Resonance 8 (1997) 17–24.

[25] S. Hafner, H.W. Spiess, Advanced solid state NMR spectroscopy of strongly dipolar coupled spins under fast magic angle spinning, Concepts in Magnetic Resonance 10 (1998) 99–128.

[26] B. Elena, G. de Paepe, L. Emsley, Direct spectral optimisation of proton–proton homonuclear dipolar decoupling in solid-state NMR, Chemical Physics Letters 398 (2004) 532–538.

[27] E. Salager, J.-N. Dumez, R.S. Stein, S. Steuernagel, A. Lesage, B. Elena-Herrmann, L. Emsley, Homonuclear dipolar decoupling with very large scaling factors for high-resolution ultrafast magic angle spinning 1H solid-state NMR spectroscopy, Chemical Physics Letters 498 (2010) 214–220.