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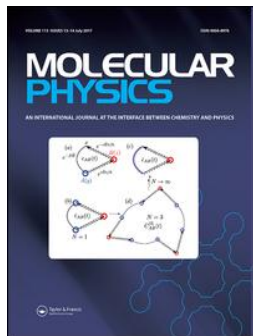
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A physical interpretation of the Floquet description of magic angle spinning nuclear magnetic resonance spectroscopy

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A physical interpretation of the Floquet description for magic angle spinning (MAS) nuclear magnetic resonance (NMR) is proposed. The effect of the spatial rotation on the spin system in sample spinning is analysed and described in terms of orbital angular momentum operators. The analogy between rotations in real space and in spin space is emphasized. The transformation properties of the irreducible tensors in real space are used to construct a Floquet Hamiltonian for MAS NMR, that is time independent and comprises one term associated with pure sample rotation. The remaining terms are associated with the spin system, and consist of spin-phonon type Floquet operators generating simultaneous transitions between rotational states and spin states. Finally, two different definitions for the Floquet density operator are compared.

1. Introduction

Magic angle spinning (MAS) nuclear magnetic resonance (NMR) is a versatile method for obtaining high resolution NMR spectra of amorphous organic solids [1]. In recent years, it has been demonstrated that MAS NMR, when combined with isotopic labelling, can be used to extract direct and high resolution molecular structural information for complex biological systems [2]. From labelled pairs specific distances or angles can be determined in membrane proteins with rotational resonance and multiple pulse sequences [3]. Recently, multidimensional MAS NMR spectroscopy on multiple labelled systems has been initiated as another strategy for resolving ordered structures in condensed phases that are inaccessible to diffraction techniques like X-ray. In a first application, a genuine membrane-associated photosynthetic light harvesting antenna was uniformly labelled ¹³C, the ¹³C and ¹H response of the antenna aggregate was fully assigned, and its structure was partially resolved [4–6]. These MAS technologies have a high potential to develop in the very near future into generic methods for the determination of ligand structure, for the characterization of ligand–protein interactions, and for comprehensive

structure determination of intrinsic membrane proteins and other membrane-bound complexes.

The initial application of multidimensional MAS NMR spectroscopy for structure refinement became possible after a convenient pulse sequence for broadband dipolar recoupling was discovered and interpreted in terms of a straightforward average Hamiltonian description for the dipolar interactions in an isolated pair of nuclear spins under MAS conditions [7]. However, it became clear that average Hamiltonian descriptions, and more generally descriptions in terms of isolated spins or pairs, are of limited use for understanding the multidimensional MAS NMR of multiple labelled systems. For the description of such experiments a more elaborate formalism is needed. This has motivated us to re-evaluate the basics and to reconsider the fundamental physics of the MAS phenomenon, aiming for a simple first-order physical interpretation for the MAS NMR in the product of real space and spin space. The description of MAS NMR experiments normally starts with the generation of a MAS spin-Hamiltonian, with time-dependent coefficients that are periodic with the spinning frequency [8]. This time-dependence complicates the simulation of MAS spectra and the description of the experimental results by a comprehensible picture.

A general approach for the description of periodically time-dependent systems can be found in the form of the Floquet theory. Shirley introduced the theorem of

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Floquet to describe the evolution of a two level system governed by a periodically time-dependent Hamiltonian [9]. To describe MAS NMR, for that purpose Floquet operators, evolution and density operators and expectation values in Floquet space were introduced [10–15]. The Floquet theory was recently reformulated into a Fourier state representation by Levante *et al.* [16]. An integral representation was given by Filip *et al.* [17] and applied to sample spinning NMR.

Another approach to treat periodically time-dependent systems is the secular averaging theory (SAT) [18]. The theory was applied to MAS by Goldman [19]. SAT was formalized by the introduction of block-operators [20]. This approach provides convenient tools to evaluate effective Hamiltonians, following an expansion procedure [21]. Llor indicated that SAT is isomorphic with the Floquet theory [20, 22]. Finally, it has been shown that Floquet theory can be combined with non-degenerate Rayleigh–Schrödinger perturbation theory by using recurrence equations to obtain corrections to the Floquet eigenvalues and eigenstates [23].

Shirley's Floquet theory is a consequence of a mathematical treatment of the Schrödinger equation with a periodically time-dependent Hamiltonian and results in a Floquet Hamiltonian represented within a set of Floquet states. Maricq proposed a method for determining the Floquet states of a forced rotor, and described the connection between Floquet states and angular momentum states [24]. Here, we propose a quantum field interpretation of the MAS NMR phenomenon by implementing an orbital angular momentum operator to describe the physics of sample rotation. This angular momentum operator is used to implement rotation around the magic angle with frequency ω_r and a reduced angular momentum. This will be used to put forward a physical interpretation of the Floquet description of MAS NMR. It appears that for all practical purposes the projection of the rotation of the entire sample onto a single set of angular momentum states is sufficient to describe the physics of the MAS. It will be shown that the operators forming the Floquet Hamiltonian are the orbital angular momentum, and ladder operators associated with variations of the rotation. The Floquet Hamiltonian is identified with the Hamiltonian in a spatial rotating frame that can be mapped onto the rotor frame. The simplification obtained from a representation within a single set of angular momentum states appears to be helpful in providing a straightforward physical interpretation of the Floquet description of MAS NMR spectroscopy, in terms of spatial irradiation and spin–phonon type interactions.

In section 2 we compare the phase representation and the orbital angular momentum representation for a forced rotation around a fixed axis. In this framework

Fourier operators are defined. In section 3 an orbital angular momentum operator is used to evaluate the transformation properties of an operator in real space. The parallels between the algebra of the operators describing spin rotations and spatial rotations are emphasized. This offers a generic framework to treat pulses and rotation in an analogous way, leading to an interpretation of the MAS effects on the spin system in terms of irradiation in real space. It is anticipated that this paradigm can and will be used in the future for constructing double resonance techniques involving radio frequency (RF) irradiation and sample rotation. In section 4 this algebra is used to describe the tensor in the real space for a rotating powder sample. It is found that a quasi-classical phase representation of the MAS NMR requires the introduction of two degrees of freedom φ', t . This contrasts with the single time degree of freedom that is sufficient to describe the interaction of the spin system with a classical rotor in the usual treatment of the MAS NMR.

In section 5 the physical interpretation of the Floquet description of the MAS NMR appears naturally. It is shown that the angular momentum representation corresponding with the quasi-classical phase representation in section 4 can be mapped onto the Floquet operator algebra that is well known in the MAS NMR. This requires the introduction of a renormalized orbital angular momentum operator, in addition to the Fourier operators, which are used to describe MAS. In this physical framework the Floquet Hamiltonian, the Floquet evolution operator, and the Floquet operators can be defined. In section 6 the expression for the density operator and the expectation value of a spin space operator in this Floquet operator formalism are introduced, while in section 7 a physical interpretation of the Floquet operators is discussed in terms of spin–phonon type operators in the product of real space and spin space. The origin of the reduced angular momentum, its associated energy, and the relation to the quasi-classical interpretation of the Floquet theory are explained in the appendix. Starting from a quantized rotor in the classical limit the eigenvalue equation for the renormalized angular momentum and the commutation relations for the Fourier operators are derived from first principles. The equivalence between an angular momentum representation within a single set of reduced angular momentum states and the quasi-classical phase representation invoked by equation (29) in section 4 is discussed. It is shown that a renormalization of the angular momentum states $|N + n\rangle \rightarrow |n\rangle$ is allowed since the matrix elements for the Fourier operators are independent of the background $|n\rangle$. It transpires that the two degrees of freedom in the phase representation are indeed essential, since the φ' leads to the correct Fourier

operators in the classical limit while the renormalization can be performed along the time degree of freedom, leading to a complete representation of the MAS within a single set of angular momentum states.

2. The forced sample rotation

During a MAS NMR experiment the sample is forced to rotate in real space around a fixed z' axis of a 'rotor angle frame' tilted at the magic angle with respect to the applied magnetic field (figure 1). The spatial rotation results in a periodic time dependence of the spin Hamiltonian of the sample. As a consequence this Hamiltonian can be expanded into Fourier series, in which each element is labelled with a Fourier number $n \in \mathbb{Z}$. In the conventional Floquet theory these Fourier expansions are used to analyse the effect of the sample rotation on the spin system [11]. This procedure is strictly mathematical with no direct relation to the physics of a rotating sample. In contrast, in this article the interaction between the spin system and the forced rotation of the sample as the source of the time-dependence is taken into account, leading to a physical interpretation of the Floquet description of MAS NMR spectroscopy.

A rotation is a canonical transformation since it replaces one set of independent spatial variables by another set [25]. The classical orbital angular momentum $R_{z'}$ is also the generator of infinitesimal rotational transformations [24, 26, 27]. Since a canonical transformation is a unitary transformation we can use a generalization of the Dirac notation for quantum mechanics to describe its physics and we define an orbital angular momentum operator $\hat{R}_{z'}$ in real space that measures the angular momentum within a set of

states $|n\rangle$ [25, 28]. In the appendix it is shown that for a quasi-classical description of differential sample rotation effects, the Fourier states $|n\rangle$ can be identified with a renormalized angular momentum, with the Fourier numbers n the eigenvalues in units of $\hbar$. In that case an eigenvalue equation for $\hat{R}_{z'}$ can be reformulated as [17, 27]

$$\hat{R}_{z'}|n\rangle = n|n\rangle. \quad (1)$$

It will be shown in the subsequent sections that in the semi-classical approximation a representation of the MAS NMR Hamiltonian exists within the set $|n\rangle$ that encompasses all the necessary physics to describe the interaction of the rotation of the macroscopic sample with the spin system. Summarizing, in this study equation (1) is a quasi-classical eigenvalue equation for the orbital angular momentum operator $\hat{R}_{z'}$, using renormalized orbital angular momentum states and eigenvalues, relative to the macroscopic value N (see the appendix).

A single spatial coordinate φ' is sufficient to describe a rotation around the fixed z' axis in the rotor angle frame. Here the subspace of the real space spanned by φ' is identified with the Fourier space in Floquet theory [17]. Since $\varphi' \in (-\pi, \pi]$ is the only spatial coordinate in this subspace, a set of phase states $\{|\varphi'\rangle\}$ can be introduced that constitutes a continuous base for the Fourier space. In that case the pair $\hat{R}_{z'}, \varphi'$ can be considered as generalized conjugate momentum and position operators for the rotation described by equation (1).

The phase representation of $|n\rangle$ and $\hat{R}_{z'}$, should lead to an expression equivalent to equation (1) in terms of φ' . The phase representation of $|n\rangle$ is [21]

$$\langle\varphi'|n\rangle = \frac{1}{2\pi^{1/2}} \exp(in\varphi'), \quad (2)$$

while the phase representation of $\hat{R}_{z'}$ yields an infinitesimal rotation in the plane perpendicular to the z axis, according to [26, 29]

$$\langle\varphi'|\hat{R}_{z'}|\vartheta'\rangle = \langle\varphi'|\vartheta'\rangle \left(-i \frac{\partial}{\partial\vartheta'}\right), \quad (3)$$

with ϑ' a rotation angle about the z' axis,

$$\langle\vartheta'|\varphi'\rangle = \delta(\vartheta - \varphi'), \quad (4)$$

according to elementary representation theory [25]. Using equations (2), (3) and (4), the phase representation of equation (1) can be verified, since

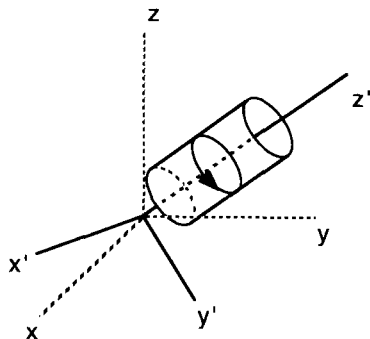


Figure 1. The forced rotation, around the z axis of the static rotor angle frame (x', y', z') in the laboratory frame (x, y, z) . A mathematical device is developed that is used to map the rotor frame on the rotor angle frame by a renormalization, while maintaining the rotational transformation properties for the macroscopic rotation in the transition operators $\hat{F}_n$.

$$\begin{aligned}
\langle \varphi' | \hat{R}_z' | n \rangle &= \int_{-\pi}^{\pi} d\vartheta' \langle \varphi' | \hat{R}_z' | \vartheta' \rangle \langle \vartheta' | n \rangle \\
&= \int_{-\pi}^{\pi} d\vartheta' \delta(\varphi' - \vartheta') \left(-i \frac{\partial}{\partial \vartheta'} \right) \\
&\quad \times \frac{1}{(2\pi)^{1/2}} \exp(in\vartheta') \\
&= n \frac{1}{(2\pi)^{1/2}} \exp(in\varphi') \\
&= n \langle \varphi' | n \rangle.
\end{aligned} \tag{5}$$

Expressing the Fourier states in terms of the phase states [24]

$$\begin{aligned}
|n\rangle &= \int_{-\pi}^{\pi} d\varphi' |\varphi'\rangle \langle \varphi' | n \rangle \\
&= \int_{-\pi}^{\pi} d\varphi' \frac{1}{(2\pi)^{1/2}} \exp(in\varphi') |\varphi'\rangle,
\end{aligned} \tag{6}$$

it is easy to show that the Fourier states are orthonormal

$$\begin{aligned}
\langle n | m \rangle &= \int_{-\pi}^{\pi} d\theta' \int_{-\pi}^{\pi} d\varphi' \frac{1}{2\pi} \exp(-i(n\varphi' - m\theta')) \delta(\varphi' - \theta') \\
&= \frac{1}{2\pi} \int_{-\pi}^{\pi} d\varphi' \exp(i(m-n)\varphi') \\
&= \delta_{nm}.
\end{aligned} \tag{7}$$

This implies that the Fourier states form a basis set for the Fourier space and that it is possible to change representation by expressing the phase states in terms of the Fourier states:

$$\begin{aligned}
|\varphi'\rangle &= \sum_{n=-\infty}^{\infty} \langle n | \varphi' \rangle |n\rangle \\
&= \sum_{n=-\infty}^{\infty} \frac{1}{(2\pi)^{1/2}} \exp(-in\varphi') |n\rangle.
\end{aligned} \tag{8}$$

The difference between the two basis sets is that the phase states constitute a continuous basis in a finite interval for the spatial coordinate $\varphi' \in (-\pi, \pi]$, while the Fourier states form an infinite discrete basis for the Fourier space with $n = -\infty \dots, \infty$.

In this Fourier space we now can define a set of Fourier operators $\hat{F}_n$ that are eigen operators of the phase states, according to [24]

$$\hat{F}_n |\varphi'\rangle = \exp(in\varphi') |\varphi'\rangle. \tag{9}$$

Some important properties of these operators can be derived from the definition in equation (9). First, they can be considered as raising and lowering operators in the Fourier states (figure 2), since [24]

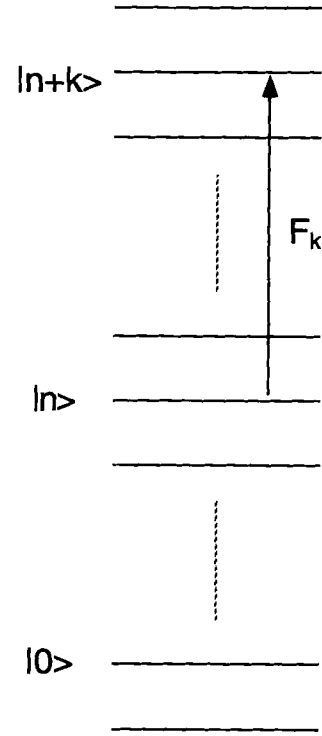


Figure 2. The sample rotation is mapped on a single manifold of Fourier states $|n\rangle$ by the renormalization. The transition operators couple between different states.

$$\begin{aligned}
\hat{F}_k |n\rangle &= \int_{-\pi}^{\pi} d\varphi' \hat{F}_k |\varphi'\rangle \langle \varphi' | n \rangle \\
&= \int_{-\pi}^{\pi} d\varphi' \exp(ik\varphi') |\varphi'\rangle \frac{1}{(2\pi)^{1/2}} \exp(in\varphi') \\
&= |n+k\rangle,
\end{aligned} \tag{10}$$

according to equations (2), (6) and (9). From this equation it follows that

$$\hat{F}_m \hat{F}_n = \hat{F}_{n+m}, \tag{11}$$

which implies that Fourier operators commute mutually, since $\hat{F}_{n+m} = \hat{F}_{m+n}$. Furthermore, equation (9) implies that the adjoint of a Fourier operator $\hat{F}_n$ is

$$\hat{F}_n^\dagger = \hat{F}_{-n}. \tag{12}$$

Finally with equations (1) and (10) the commutation relation

$$[\hat{R}_z', \hat{F}_n] = n\hat{F}_n \tag{13}$$

between $\hat{R}_z'$ and $\hat{F}_n$ can be derived.

When the operators $\hat{F}_n$ are represented within the set of renormalized angular momentum states, they generate $\{|n\rangle\}$ from $|0\rangle$. In the appendix we show that when the full angular momentum states are used instead, the equivalent of the $\hat{F}_n$ operators are

the creation and annihilation operators $\hat{a}, \hat{a}^\dagger$ enabling the exchange of energy between the spin system and the rotor bath in a quasi-classical quantum mechanical description of the MAS NMR phenomenon.

So far we have introduced two possible representations for the states and the operators in the Fourier space: the phase and the angular momentum representation defined by the basis sets $\{|\varphi'\rangle\}$ and $\{|n\rangle\}$ respectively. The relationships between the two representations were verified. In the next sections these operators and their relations will be used to describe MAS NMR experiments.

3. Transformations in spin space and real space

The Hamiltonian, which is the operator associated with the energy of the spin system, consists in the case of NMR of a spatial part and a spin part. Therefore the MAS NMR Hamiltonian is conveniently expressed in terms of contractions between $\hat{\mathbf{A}}_k$, the irreducible tensor operators of rank k in real space, and $\hat{\mathbf{T}}_k$, the irreducible tensor operators of rank k in spin space, according to [18, 30]

$$\hat{\mathcal{H}}_S = \sum_k \sum_{q=-k}^{+k} (-1)^q \hat{A}_{kq} \hat{T}_{k(-q)}. \quad (14)$$

This semi-classical Hamiltonian describes the interaction of the spin system with its surrounding. The spin part of this Hamiltonian is most effectively described quantum mechanically, while the spatial part is usually described classically. The elements of both the $\hat{\mathbf{A}}_k$ and the $\hat{\mathbf{T}}_k$ operators satisfy the irreducible tensor transformation properties [30]. $\hat{\mathbf{T}}_k$ can be transformed by a spin angular momentum operator $\hat{\mathbf{I}}$, while the transformation of $\hat{\mathbf{A}}_k$ requires an orbital angular momentum operator $\hat{\mathbf{R}}$, with components $\hat{R}_x$, $\hat{R}_y$ and $\hat{R}_z$.

In spin space a rotational transformation in the $\mathbf{n}$ -direction of an arbitrary spin-operator $\hat{Q}_S$ into $\hat{Q}_S^1$ is described by [29]

$$\hat{Q}_S^1 = \exp(i\theta(\mathbf{n} \cdot \hat{\mathbf{I}})) \hat{Q}_S \exp(-i\theta(\mathbf{n} \cdot \hat{\mathbf{I}})), \quad (15)$$

where the components of $\hat{\mathbf{I}}$ satisfy the commutation relation

$$[\hat{I}_x, \hat{I}_y] = i\hat{I}_z, \quad (16)$$

and its cyclic permutation [27].

The irreducible tensor operators $\hat{\mathbf{T}}_k$ are defined by the commutation rules of their elements with the elements of the spin angular momentum operator, according to [27, 30]

$$[\hat{I}_z, \hat{T}_{kq}] = q\hat{T}_{kq},$$

$$[\hat{I}_\pm, \hat{T}_{kq}] = [(k \mp q)(k \pm q + 1)]^{1/2} \hat{T}_{k(q \pm 1)}, \quad (17)$$

with $q = -k, \dots, k$. The transformation properties for a three-dimensional rotation in spin space, defined by the spin rotation operator [29]

$$\hat{\mathcal{R}}_I(\alpha, \beta, \gamma) = \exp(i\alpha\hat{I}_z) \exp(i\beta\hat{I}_y) \exp(i\gamma\hat{I}_z), \quad (18)$$

of the elements of $\hat{\mathbf{T}}_k$ are determined by the Wigner rotation matrix elements [18]

$$\begin{aligned} \hat{T}_{kq}^1 &= \hat{\mathcal{R}}_I(\alpha, \beta, \gamma) \hat{T}_{kq} \hat{\mathcal{R}}_I^{-1}(\alpha, \beta, \gamma) \\ &= \sum_{p=-k}^k \hat{T}_{kp} D_{pq}^k(\alpha, \beta, \gamma), \end{aligned} \quad (19)$$

where (α, β, γ) are the Euler angles of the rotation.

By analogy, rotational transformations of an operator $\hat{Q}'_R$ into $\hat{Q}_R$ in real space can be performed, by using an orbital angular momentum operator $\hat{\mathbf{R}}$, which is the generator of the infinitesimal rotational transformations in real space. This canonical transformation is described by an unitary operator, according to

$$\hat{Q}_R = \exp(i\theta(\mathbf{n} \cdot \hat{\mathbf{R}})) \hat{Q}'_R \exp(-i\theta(\mathbf{n} \cdot \hat{\mathbf{R}})), \quad (20)$$

with

$$[\hat{R}_{x'}, \hat{R}_{y'}] = i\hat{R}_{z'}, \quad (21)$$

and its cyclic permutations [29]. The elements of the irreducible tensor operator $\hat{\mathbf{A}}_k$ in real space are defined, in analogy to equation (17), by commutation relations with the elements of $\hat{\mathbf{R}}$ [27, 30]

$$\begin{aligned} [\hat{R}_{z'}, \hat{A}'_{kq}] &= q\hat{A}'_{kq}, \\ [\hat{R}_{\pm'}, \hat{A}'_{kq}] &= [(k \mp q)(k \pm q + 1)]^{1/2} \hat{A}'_{k(q \pm 1)}. \end{aligned} \quad (22)$$

The transformation properties for a three-dimensional rotation in real space are defined by the spatial rotation operator [28]

$$\hat{\mathcal{R}}_R(\alpha', \beta', \gamma') = \exp(i\alpha'\hat{R}_{z'}) \exp(i\beta'\hat{R}_{y'}) \exp(i\gamma'\hat{R}_{x'}), \quad (23)$$

and are given by [29]

$$\begin{aligned} \hat{A}_{kq} &= \hat{\mathcal{R}}_R(\alpha', \beta', \gamma') \hat{A}'_{kq} \hat{\mathcal{R}}_R^{-1}(\alpha', \beta', \gamma') \\ &= \sum_{p=-k}^k \hat{A}'_{kp} D_{pq}^k(\alpha', \beta', \gamma'). \end{aligned} \quad (24)$$

Hence there exists a general analogy between rotations in real space and in spin space. In the next sections this analogy will be utilized for the description of MAS NMR spectroscopy. In addition, since the application of a RF pulse on a spin system can be expressed as a

rotational transformation of its spin angular momentum, the analogy between equations (15) and (20) implies that sample rotation can be expressed in the Hamiltonian as an 'irradiation' term inducing a canonical transformation in real space [31].

4. Sample rotations in real space

The rotational transformation properties of the elements of the $\hat{A}_k$ tensor in the MAS Hamiltonian are given in equation (24). These elements are a function of the polar coordinates (θ, φ) in the axis system in which the tensor is defined. Transformations between coordinate systems result in a dependence of the tensor elements on the Euler angles, defining the relative orientations of the corresponding axis systems, $\hat{A}_{kq} = A_{kq}(\alpha, \beta, \gamma)$ [32]. Similarly, a forced rotation of the sample around the z' axis of the rotor angle frame results in a time dependence of these elements. In this section we derive the time dependence of the elements of A_k . The description uses two degrees of freedom, the time t and the spatial coordinate φ' that have already been introduced in section 2. This is used in the next section, where the spatial part of the Hamiltonian (14) is treated analogous to its spin part.

For sample spinning NMR there are in general three spatial canonical transformations necessary in transforming a tensor operator $\hat{A}_k$, defined in its own principal axis system (PAS), via the crystal frame and the rotor frame to the laboratory frame [18]. To provide first the angular dependence of the spatial part of the Hamiltonian of a static crystallite, we use the following three successive transformations:

$$A_{kq}''' \xrightarrow{(\alpha''', \beta''', \gamma''')} A_{kq}'' \xrightarrow{(\alpha'', \beta'', \gamma'')} A_{kq}' \xrightarrow{(\alpha', \beta', \gamma')} A_{kq} \quad (25)$$

(i) a transformation from the PAS (x''', y''', z''') to a crystal frame, with $(\alpha''' = \alpha_p, \beta''' = \beta_p, \gamma''' = \gamma_p)$ the Euler angles of the PAS in a fixed molecular frame in the crystallite; (ii) a transformation from the crystal frame (x'', y'', z'') to the fixed rotor angle frame, with $(\alpha'' = \alpha_c, \beta'' = \beta_c, \gamma'' = \gamma_c)$ the Euler angles of the crystal frame in the rotor angle frame; and (iii) a transformation from the rotor angle frame (x', y', z') to the laboratory frame (x, y, z), with $(\alpha' = \varphi_0, \beta' = \beta_r, \gamma' = \gamma_r)$. The angle φ_0 can be chosen arbitrarily and fixes the direction of the x' axis of the rotor angle frame in the laboratory frame.

The elements of the tensor in the laboratory frame A_k can be expressed in terms of the elements of the tensor in the rotor angle frame A_k' , which in turn are functions of the spatial coordinate φ' . The elements of $\hat{A}_k$ can now be written as a function of the spatial coordinate φ' of the rotor angle frame:

$$\begin{aligned} A_{kq}(\varphi') &= \sum_{p=-k}^k A_{kp}'(\varphi') D_{pq}^k(\varphi_0, \beta_r, \gamma_r) \\ &= \sum_{p=-k}^k \exp(ip\varphi') A_{kp}'(0) D_{pq}^k(\varphi_0, \beta_r, \gamma_r) \end{aligned} \quad (26)$$

according to equation (25). Here we use that A_{kp}' depends on the spatial coordinate φ' in the rotor angle frame according to $A_{kp}'(\varphi') = \exp(ip\varphi') A_{kp}'(0)$ [33]. This implies that the coefficients $\exp(ip\varphi')$ in the expansion of the tensor elements of A_{kq}' in the laboratory frame in equation (26) represent the explicit dependence of the spin-Hamiltonian in equation (14) on the spatial coordinate φ' . As a result operators and state functions in the laboratory frame will depend on φ' . In particular, observables and Hamiltonians can be calculated formally as a function of φ' , which represents the first degree of freedom. The important point is that φ' introduces the transformation properties for rotations around the z' axis of the rotor angle frame in the phase representation into the theoretical description. The functional dependence on φ' will be explored to generate the interaction with the spins and φ' will be assigned a constant value afterwards, which implies that the variation $\Delta\varphi' \rightarrow 0$.

Using the overall transformation for a static sample from the PAS to the laboratory frame equation (26) can be reformulated, using the equations (23)–(25), as

$$A_{kq}(\varphi') = \sum_{p=-k}^k \exp(ip\varphi') V_{pq}^k, \quad (27)$$

with

$$\begin{aligned} V_{pq}^k &= \sum_{s=-k}^k \sum_{r=-k}^k A_{kr}''' D_{rs}^k(\alpha_p, \beta_p, \gamma_p) D_{sp}^k(\alpha_c, \beta_c, \gamma_c) \\ &\quad \times D_{pq}^k(\varphi_0, \beta_r, \gamma_r). \end{aligned} \quad (28)$$

All Euler angles of the transformations are included in the V_{pq}^k coefficients.

Next we introduce a second degree of freedom associated with the forced rotation of the sample by the application of a time-dependent canonical transformation in real space. The axis of rotation is in the direction of the z' axis of the rotor angle frame. Thus a convenient way of evaluating the expression for the A_{kq} elements in the laboratory frame is to replace φ_0 by a time dependent term $\varphi_0 + \omega_r t$. Separating the rotation from the expressions in equations (27) and (28) by writing it explicitly, we obtain

$$\begin{aligned}
A_{kq}(\varphi', t) &= \sum_{p=-k}^k \exp(ip(\omega_r t + \varphi')) V_{pq}^k \\
&= \exp\left(i\omega_r \left(-i \frac{\partial}{\partial \varphi'}\right) t\right) A_{kq}(\varphi', 0) \\
&\quad \times \exp\left(-i\omega_r \left(-i \frac{\partial}{\partial \varphi'}\right) t\right), \quad (29)
\end{aligned}$$

which can be shown by Taylor expansion [26].

The elements of the second rank tensor $k = 2$, describing the coefficients of the chemical shift or dipolar interaction in a spin system, are in their principal axis system equal to [32]

$$\begin{aligned}
A''_{00} &= \bar{A} \\
A''_{20} &= \left(\frac{3}{2}\right)^{1/2} \delta \\
A''_{2\pm 2} &= \frac{1}{2} \eta \delta \quad (30)
\end{aligned}$$

with $\bar{A} = \frac{1}{3} \text{Tr}\{\mathbf{A}\}$ the isotropic part, $\delta = A_{zz} - \bar{A}$ the anisotropy parameter, and $\eta = (A_{yy} - A_{xx})/\delta$ the asymmetry parameter of the interaction. The values of these parameters must be inserted in equation (28) for the evaluation of the V_{pq}^k parameters.

In the MAS case the angle β_r between the axis of rotation and the external magnetic field is equal to the magic angle $\beta_r = \beta_m$ with $d_{00}^2(\beta_m) = 0$. This condition enables the performance of high-resolution NMR experiments of solids [34].

5. The Floquet Hamiltonian

In this section we discuss the form of the MAS Hamiltonian in Floquet space. This space is defined as the product space of the Fourier and the spin space [16]. The Fourier operators $\hat{F}_n$ and the orbital angular momentum operator $\hat{R}_{z'}$ are defined in Fourier space, while the spin angular momentum operators $\hat{I}_x$, $\hat{I}_y$ and $\hat{I}_z$ are defined in spin space. In the product space Floquet operators can be introduced that are products of Fourier and spin operators.

The time t and the spatial coordinate φ' in equation (29) are the two degrees of freedom that are necessary for the description of the MAS experiments presented in this paper.

The semi-classical Hamiltonian defined in equation (14) can be rewritten, using equation (29), according to,

$$\hat{\mathcal{H}}_S(\varphi', t) = \exp\left(i\omega_r \left(-i \frac{\partial}{\partial \varphi'}\right) t\right) \sum_{q=-k}^k (-1)^q$$

$$\begin{aligned}
&\times A_{kq}(\varphi', 0) \hat{T}_{k(-q)} \exp\left(-i\omega_r \left(-i \frac{\partial}{\partial \varphi'}\right) t\right) \\
&= \exp\left(i\omega_r \left(-i \frac{\partial}{\partial \varphi'}\right) t\right) \hat{\mathcal{H}}_S(\varphi', 0) \\
&\quad \times \exp\left(-i\omega_r \left(i \frac{\partial}{\partial \varphi'}\right) t\right), \quad (31)
\end{aligned}$$

with $\hat{\mathcal{H}}_S(\varphi', 0)$ the Hamiltonian at $t = 0$, which is equal to the static Hamiltonian obtained from the insertion of the expressions for the tensor elements in equation (27):

$$\hat{\mathcal{H}}_S(\varphi', 0) = \sum_{q=-2}^2 \sum_{p=-2}^2 \exp(ip\varphi') V_{pq}^k \hat{T}_{k(-q)}. \quad (32)$$

The time-dependent semi-classical spin Hamiltonian $\hat{\mathcal{H}}_S(\varphi', t)$ in equation (32) governs the time evolution of the spin state functions $|\psi_S(\varphi', t)\rangle$ of the spin system, according to the Schrödinger wave equation of motion:

$$\frac{d}{dt} |\psi_S(\varphi', t)\rangle + i\hat{\mathcal{H}}_S(\varphi', t) |\psi_S(\varphi', t)\rangle = 0. \quad (33)$$

Both $\hat{\mathcal{H}}_S(\varphi', t)$ and $|\psi_S(\varphi', t)\rangle$ in the laboratory frame are functions of the spatial coordinate φ' . Hence, equation (31) can be considered as the phase representation of the Schrödinger equation in Floquet space,

$$\frac{d}{dt} |\psi_S^{\mathcal{F}}(t)\rangle + i\hat{\mathcal{H}}_S^{\mathcal{F}}(t) |\psi_S^{\mathcal{F}}(t)\rangle = 0, \quad (34)$$

where the phase representation of the spin Floquet Hamiltonian $\hat{\mathcal{H}}_S^{\mathcal{F}}(t)$ is given by

$$\langle \varphi' | \hat{\mathcal{H}}_S^{\mathcal{F}}(t) | \vartheta' \rangle = \hat{\mathcal{H}}_S(\varphi', t) \delta(\varphi' - \vartheta'). \quad (35)$$

The spin Floquet Hamiltonian $\hat{\mathcal{H}}_S^{\mathcal{F}}(t)$ can be written, using equations (3), (32) and (35), as

$$\hat{\mathcal{H}}_S^{\mathcal{F}}(t) = \exp(i\omega_r \hat{R}_{z'} t) \hat{\mathcal{H}}_S^{\mathcal{F}}(0) \exp(-i\omega_r \hat{R}_{z'} t). \quad (36)$$

Here the time-dependence is given explicitly and the time-independent Hamiltonian

$$\hat{\mathcal{H}}_S^{\mathcal{F}}(0) = \sum_k \sum_{q=-k}^k \sum_{p=-k}^k (-1)^q \hat{F}_p V_{pq}^k \hat{T}_{k(-q)}, \quad (37)$$

according to equations (9), (33) and (35). The time dependence in equation (36) is represented by the canonical transformation operator $\exp(i\omega_r \hat{R}_{z'} t)$, in which the orbital angular momentum operator $\hat{R}_{z'}$ is the generator of the infinitesimal rotations around the z' axis. For a static sample $\omega_r = 0$ and the Hamiltonian $\hat{\mathcal{H}}_S^{\mathcal{F}}(0)$ governs the evolution of the spin system. For $\omega_r \neq 0$, the interaction between the sample spinning and the spin system is included here via the semi-classical rotational transformation properties introduced with the φ' coordinate in the phase representation. It

is represented in $\mathcal{H}_S^{\mathcal{F}}$ ($\mathcal{O}$), through the Fourier operators $\hat{F}_p$ in equation (37).

The time evolution of the spin state function in the phase representation is given by

$$|\psi_S(\varphi', t)\rangle = \hat{U}_S(\varphi', t)|\psi_S(\varphi', 0)\rangle. \quad (38)$$

$U_S(\varphi', t)$ is a spin evolution operator in the laboratory frame and is a function of the spatial coordinate φ' of the rotor angle frame. The time evolution of the spin Floquet state function can be evaluated, using

$$|\psi_S^{\mathcal{F}}(t)\rangle = \hat{U}_S^{\mathcal{F}}(t)|\psi_S^{\mathcal{F}}(0)\rangle. \quad (39)$$

Here $U_S^{\mathcal{F}}(t)$ is the spin Floquet evolution operator, related to $U_S(\varphi', t)$ via

$$\langle\varphi'|\hat{U}_S^{\mathcal{F}}(t)|\vartheta'\rangle = \hat{U}_S(\varphi', t)\delta(\varphi' - \vartheta'). \quad (40)$$

The equation for the time evolution of the spin Floquet evolution operator can be obtained by substitution of equation (39) in equation (31), yielding

$$\frac{d}{dt} \hat{U}_S^{\mathcal{F}}(t) + i\hat{\mathcal{H}}_S^{\mathcal{F}}(t)\hat{U}_S^{\mathcal{F}}(t) = 0. \quad (41)$$

The time-dependence of the spin Floquet Hamiltonian makes it difficult to solve this equation. To overcome this difficulty, the special form of the Hamiltonian in equation (36) allows transformation to a spatial rotating frame.

In NMR spectroscopy it is common to transform a spin Hamiltonian to the spin rotating frame, in particular when the RF irradiation

$$H_1 \exp(-i\omega_0 \hat{I}_z t) \hat{I}_x \exp(i\omega_0 \hat{I}_z t)$$

term makes the laboratory Hamiltonian time dependent. In that case a transformation of the form $\exp(i\omega_0 \hat{I}_z t)$ generates a time independent spin rotating frame Hamiltonian that rotates about the z axis of the laboratory frame [35]. In the same way the time dependent spin Floquet Hamiltonian $\mathcal{H}_S^{\mathcal{F}}(t)$ in equation (36) can be transformed using the operator $\exp(-i\omega_r \hat{R}_z t)$ to generate the Hamiltonian in a spatial rotating frame. This frame rotates about the z' axis of the rotor angle frame with a rotor frequency ω_r and can be identified with the rotor frame in the MAS NMR. If the Hamiltonian is represented with respect to the single set $|n\rangle$ around $|0\rangle$, its energy is renormalized (see the appendix). The semiclassical interaction with the spin system is fully retained in the $\hat{F}_n$ operators and their functional dependence on φ' .

After transformation of equation (41) to the rotor frame, another Floquet Hamiltonian $\hat{\mathcal{H}}^{\mathcal{F}}$ is obtained, satisfying

$$\frac{d}{dt} \hat{U}^{\mathcal{F}}(t) + i\hat{\mathcal{H}}^{\mathcal{F}} \hat{U}^{\mathcal{F}}(t) = 0, \quad (42)$$

with $\hat{U}^{\mathcal{F}}(t) = \hat{U}_R^{\mathcal{F}}(t) \hat{U}_S^{\mathcal{F}}(t)$, and

$$\hat{U}_R^{\mathcal{F}}(t) = \exp(i\omega_r \hat{R}_z t). \quad (43)$$

$\hat{\mathcal{H}}^{\mathcal{F}}$ is now time independent and the solution of equation (42) is

$$\hat{U}^{\mathcal{F}}(t) = \exp(-i\hat{\mathcal{H}}^{\mathcal{F}} t). \quad (44)$$

At this stage, it is of interest to point out the parallel with the early treatment given by Shirley. According to equation (40), the dependence of the spin evolution operator $\hat{U}_S(\varphi', t)$ on $\hat{U}_S^{\mathcal{F}}(t)$ is

$$\hat{U}_S(\varphi', t) = \int_{-\pi}^{\pi} d\vartheta' \langle\varphi'|\hat{U}_S^{\mathcal{F}}(t)|\vartheta'\rangle, \quad (45)$$

which can be expressed within the set of Fourier states, yielding

$$\begin{aligned} \hat{U}_S(\varphi', t) &= \int_{-\pi}^{\pi} d\vartheta' \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{1}{2\pi} \exp(-i(m\vartheta' - n\varphi')) \\ &\quad \times \langle n|\hat{U}_R^{\mathcal{F}}(t)\hat{U}_S^{\mathcal{F}}(t)|m\rangle \\ &= \sum_{n=-\infty}^{\infty} \exp(in(\omega_r t + \varphi')) \langle n|\hat{U}^{\mathcal{F}}(t)|0\rangle, \end{aligned} \quad (46)$$

using equations (8) and (40). For $\varphi' = 0$ this equation matches Shirley's expression for the connection between the spin and Floquet evolution operators [9].

The time-independent Floquet Hamiltonian in equation (42) has the form

$$\hat{\mathcal{H}}^{\mathcal{F}} = \hat{\mathcal{H}}_S^{\mathcal{F}} + \hat{\mathcal{H}}_R^{\mathcal{F}} \quad (47)$$

with $\hat{\mathcal{H}}_S^{\mathcal{F}}(t) = \hat{\mathcal{H}}_S^{\mathcal{F}}(0)$ in equation (37) and

$$\hat{\mathcal{H}}_R^{\mathcal{F}} = \omega_r \hat{R}_z. \quad (48)$$

With respect to its rotational transformation properties, this term can be compared with the $-\omega_0 \hat{I}_z$ term in spin rotating frame Hamiltonians. The energy associated with a macroscopic sample rotation is very large compared to the nuclear interactions, and the spinning speed is forced to be constant and will not change through the energy exchange of the sample with the spin system. However, since ω_r is finite and the Hamiltonian will be represented within the set of reduced angular momentum states $|n\rangle$, the rotational energy associated with $\hat{\mathcal{H}}_R^{\mathcal{F}}$ will be comparable with the other frequency terms in the Hamiltonian. Since $[\hat{R}_z, \hat{F}_n] = n\hat{F}_n$ the commutator of $\hat{\mathcal{H}}_R^{\mathcal{F}}$ and $\hat{\mathcal{H}}_S^{\mathcal{F}}$ does not vanish. Consequently, $\hat{\mathcal{H}}_S^{\mathcal{F}}$ couples between states differing in their orbital rotation quantum number n via the ladder operators $\hat{F}_n$ in a non-secular type term $\hat{\mathcal{H}}_S^{\mathcal{F}}$. In a general description of the motions of the N_0 nuclei in a crystal, their positions can be described in terms of $3N_0$ normal coordinates or acoustic phonon modes. Exactly 6 of the N_0 coordinates represent the translational and

rotational degrees of freedom of the entire lattice. From this perspective, $\hat{\mathcal{H}}_S^{\mathcal{F}}$ represents a spin-phonon type interaction.

Insight into the effect of the sample rotation on the Hamiltonian is obtained by making a comparison between $\hat{\mathcal{H}}^{\mathcal{F}}$ in equation (47) and the Hamiltonian $\hat{\mathcal{H}}$ associated with a static spin system, exposed to spin lock RF irradiation in the x direction [16]

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_S + \hat{\mathcal{H}}_{\text{RF}}, \quad (49)$$

with the RF Hamiltonian

$$\hat{\mathcal{H}}_{\text{RF}} = \omega_1 \hat{I}_x. \quad (50)$$

In the spin rotating frame the $\hat{\mathcal{H}}_{\text{RF}}$ generates a small Zeeman splitting just as $\omega_1 \hat{I}_x$ creates a manifold of equally spaced spin states, the $\hat{\mathcal{H}}_R^{\mathcal{F}}$ creates a manifold of rotational states.

We conclude that for all practical purposes the introduction of $\hat{R}_z$ and the ladder operators $\hat{F}_n$ is sufficient to describe the physics of the MAS NMR. It is primarily the rotational transformation properties that are of importance for the description of the MAS NMR, in agreement with expectations and the considerations in the appendix. The analogy between the formulas in equations (47) and (49) implies that the sample spinning can be interpreted as an ‘irradiation’ field acting on the spatial part of the spin system in the spatial rotating frame. The strength of the ‘irradiation’ is proportional to the spinning speed.

The total Floquet Hamiltonian for a spin system, rotating at the magic angle and experiencing a continuous RF field can thus be written as:

$$\hat{\mathcal{H}}_T^{\mathcal{F}} = \hat{\mathcal{H}}_S^{\mathcal{F}} + \hat{\mathcal{H}}_R^{\mathcal{F}} + \hat{\mathcal{H}}_{\text{RF}}^{\mathcal{F}}. \quad (51)$$

This $\hat{\mathcal{H}}_T^{\mathcal{F}}$ paves the way for a more comprehensive description of spin and space rotations simultaneously, and may lead to a first-order quasi-classical approximation of spin-phonon type interactions for multi-spin dipolar coupled networks.

The $\hat{\mathcal{H}}^{\mathcal{F}}$ Hamiltonian in equation (47) can also be represented with respect to the Fourier states. To do so we expand the Floquet Hamiltonian in its Fourier components according to equation (37).

$$\hat{\mathcal{H}}^{\mathcal{F}} = \sum_{p=-\infty}^{+\infty} \hat{F}_p \hat{\mathcal{H}}^p + \omega_r \hat{R}_{z'}, \quad (52)$$

with $\hat{\mathcal{H}}^p$ the Fourier components of the spin Hamiltonian $\hat{\mathcal{H}}_S(0,0)$

$$\hat{\mathcal{H}}^p = \sum_k \sum_{q=-k}^k (-1)^q V_{pq}^k \hat{T}_{k(-q)}. \quad (53)$$

In the representation with respect to the Fourier states, which are here reduced orbital angular momentum

states, the matrix elements of the Floquet Hamiltonian are of the form:

$$\langle n | \hat{\mathcal{H}}^{\mathcal{F}} | m \rangle = \hat{\mathcal{H}}^{n-m} + n\omega_r \delta_{nm}, \quad (54)$$

according to equations (1) and (10). These correspond to the elements of Shirley’s Floquet Hamiltonian [9] and the energy scale of the diagonal elements is set by ω_r as before.

If the Fourier spin operators $\hat{\mathcal{H}}^p$ are linear in the spin operators $\hat{I}_\lambda$, they can be written in the form

$$\hat{\mathcal{H}}^p = \sum_{\lambda} z_{p\lambda} \hat{I}_\lambda, \quad (55)$$

with $z_{p\lambda}$ complex coefficients defined by the coefficients of equation (37). Substitution of equation (55) into equation (52) leads to an operational form of the Floquet Hamiltonian

$$\hat{\mathcal{H}}^{\mathcal{F}} = \sum_{\lambda} \sum_{p=-\infty}^{+\infty} z_{p\lambda} \hat{G}_{p\lambda} + \omega_r \hat{R}_{z'}. \quad (56)$$

In this expansion we introduced the Floquet space operators

$$\hat{G}_{n\lambda} \equiv \hat{F}_n \hat{I}_\lambda, \quad (57)$$

that operate both in real space and spin space. For $\lambda = x, y, z$ these Floquet operators obey the commutation relations

$$[\hat{G}_{nx}, \hat{G}_{my}] = i\hat{G}_{(m+n)z}, \quad (58)$$

and their cyclic permutations in x, y and z , according to equations (11) and (16). Their products satisfy

$$\hat{G}_{(n+m)\alpha} \hat{G}_{-m\beta} = \hat{G}_{n\alpha} \hat{G}_{0\beta} \quad (59)$$

for all m values. The form of the Floquet Hamiltonian in equation (56) resembles the operational form of the Floquet Hamiltonian used by Zax *et al.* [15] and Schmidt and Vega [13]. However, in our case the operators correspond to actual orbital angular momentum operators and ladder operators in Fourier space, while Zax *et al.* [15] introduced these operators by defining their non-zero matrix elements.

6. The Floquet density operator

The time-evolution of the spin system is in general expressed by the time evolution of its spin-density operator in spin space. In the MAS NMR case a spin density operator

$$\hat{\rho}_S(\varphi', t) = |\psi_S(\varphi', t)\rangle \langle \psi_S(\varphi', t)| \quad (60)$$

can be defined, where φ' is the spatial coordinate introduced in section 2 [36]. The general form for the φ' -dependence of the spin state function $|\psi_S(\varphi', t)\rangle$ can be derived from the $U_S(\varphi', t)\hat{U}^{\mathcal{F}}(t)$ in equation (46). It can

be expanded with respect to a basis in spin space $\{|\sigma_i\rangle\}$ with φ' -dependent coefficients.

$$\begin{aligned} |\psi_S(\varphi', t)\rangle &= \sum_i c_i(\varphi', t) |\sigma_i\rangle \\ &= (2\pi)^{1/2} \sum_i \sum_{n=-\infty}^{\infty} c_{ni}(t) \frac{1}{(2\pi)^{1/2}} \\ &\quad \times \exp(in(\omega_r t + \varphi')) |\sigma_i\rangle. \end{aligned} \quad (61)$$

The explicit φ' -dependence of the density operator can be found by substituting equation (61) in equation (60), according to

$$\begin{aligned} \hat{\rho}_S(\varphi', t) &= \sum_{i,j} \sum_{k,l=-\infty}^{\infty} c_{li}(t) c_{kj}^*(t) \exp(i(l-k) \\ &\quad \times (\omega_r t + \varphi')) |\sigma_i\rangle \langle \sigma_j| \\ &= \sum_{n=-\infty}^{\infty} \rho_{Sn}(t) \exp(in(\omega_r t + \varphi')), \end{aligned} \quad (62)$$

with Fourier components

$$\hat{\rho}_{Sn}(t) = \sum_{i,j} \sum_{k=-\infty}^{\infty} c_{n+ki}(t) c_{kj}^*(t) |\sigma_i\rangle \langle \sigma_j|. \quad (63)$$

There are different ways to construct the Floquet density operator from equation (62). Two different approaches were reported and will be discussed here. First, the approach of Levante *et al.* [16] will be discussed, and their approach will be compared with the approach of Weintraub and Vega [14].

The Floquet density operator according to Levante *et al.* is defined by replacing the exponents in equation (62) by their Fourier states [16]

$$\hat{\rho}^{\mathcal{F}}(t) = \sum_{i,j} \sum_{k,l=-\infty}^{\infty} c_{li}(t) c_{kj}^*(t) |\sigma_i l\rangle \langle \sigma_j k|, \quad (64)$$

according to equation (2). The relation between the density operator and the Floquet density operators is then given by

$$\hat{\rho}(\varphi', t) = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \exp(i(n-m)(\omega_r t + \varphi')) \langle n | \hat{\rho}^{\mathcal{F}}(t) | m \rangle, \quad (65)$$

which can easily be verified by substitution of equation (64) into equation (65).

This expression for the density operator can be used to calculate the expectation value of an operator $\langle \hat{I}_\lambda \rangle$ in the spin space: $\langle \hat{I}_\lambda \rangle$ is evaluated by a trace of the form [36]

$$\langle I_\lambda \rangle = \text{Tr} \{ \hat{I}_\lambda \hat{\rho}(\varphi', t) \}. \quad (66)$$

Insertion of the expression for the spin density in equation (66) yields

$$\begin{aligned} \langle I_\lambda \rangle &= \text{Tr} \left\{ \sum_{m=-\infty}^{\infty} \langle m | \left[\sum_{k=-\infty}^{\infty} \hat{I}_\lambda \hat{F}_k \exp(-ik\omega_r t) \right] \hat{\rho}^{\mathcal{F}}(t) | m \rangle \right\} \\ &= \text{Tr} \{ \hat{I}_\lambda^{\mathcal{F}}(t) \hat{\rho}^{\mathcal{F}}(t) \}, \end{aligned} \quad (67)$$

where equation (10) was used and the operator in the spatial rotating frame $\hat{I}_\lambda^{\mathcal{F}}(t)$ is

$$\hat{I}_\lambda^{\mathcal{F}}(t) = \sum_{k=-\infty}^{\infty} \hat{G}_{k\lambda} \exp(-ik\omega_r t). \quad (68)$$

The trace in equation (68) is the sum of all diagonal elements of the product operators in Floquet space. In equation (67) we have finally set $\varphi' = 0$, in order to avoid redundant transformations.

Another definition of the Floquet density operator was introduced by Weintraub and Vega [14]. In their case the Floquet density operator is constructed from the spin density operator given in equation (62) using the Fourier operators defined in equation (9):

$$\hat{\rho}^{\mathcal{F}}(t) = \sum_{n=-\infty}^{\infty} \hat{\rho}_{Sn}(t) \hat{F}_n. \quad (69)$$

Since the Fourier operators obey the relation $\langle n | \hat{F}_p | m \rangle = \langle n+k | \hat{F}_p | m+k \rangle$, this Floquet density operator has the same band structure. It is easy to show that the relationship between the Floquet density operator and the spin density operator is given by,

$$\hat{\rho}_S(\varphi', t) = \sum_{n=-\infty}^{\infty} \exp(in(\omega_r t + \varphi')) \langle n | \hat{\rho}^{\mathcal{F}}(t) | 0 \rangle. \quad (70)$$

Insertion of the expression for the spin density operator in equation (66) yields,

$$\begin{aligned} \langle I_\lambda \rangle &= \text{Tr} \left\{ \langle 0 | \left[\sum_{k=-\infty}^{\infty} \hat{I}_\lambda \hat{F}_k \exp(-ik\omega_r t) \right] \hat{\rho}^{\mathcal{F}}(t) | 0 \rangle \right\} \\ &= \text{Tr} \{ \langle 0 | \hat{I}_\lambda^{\mathcal{F}}(t) \hat{\rho}^{\mathcal{F}}(t) | 0 \rangle \}, \end{aligned} \quad (71)$$

where the trace requires a summation only over the spin state diagonal elements and $\varphi' = 0$.

The main difference between the expressions for the expectation values in equations (67) and (71), is that in equation (71) only one matrix element in the Fourier space is taken into account, while equation (67) involves the summation over all diagonal elements in Fourier space. The matrix elements of the density operator, according to the definition of the Floquet density operator by Weintraub and Vega [14], satisfy the condition $\langle n | \hat{\rho}^{\mathcal{F}}(t) | m \rangle = \langle n+k | \hat{\rho}^{\mathcal{F}}(t) | m+k \rangle$ for all k , while the definition of Levante *et al.* [16] does not incorporate this band structure in the Floquet density operator. As a

result of this difference the trace in equation (67) is over all Fourier state diagonal elements, while in equation (71) only the diagonal elements with respect to the spin states are summed together.

7. Discussion and conclusions

In this publication we have proposed a physical interpretation of the Floquet theory that is used to describe MAS NMR experiments. The introduction of the phase representation of the Hamiltonian allowed the introduction of an orbital angular momentum operator $\hat{R}_{z'}$, and the definition of Fourier ladder operators $\hat{F}_n$. This made it possible to construct a spin Floquet Hamiltonian, containing the orbital angular momentum operator $\hat{R}_{z'}$, and the Floquet operators $\hat{G}_{n\lambda}$. With the proper transformations a time independent Floquet Hamiltonian, which is the Hamiltonian in the spatial rotating frame, was obtained that is equivalent to the Floquet Hamiltonian already utilized in MAS NMR. In our Hamiltonian the Floquet operators are representing the angular momentum operators and ladder operators. It can be concluded that the Floquet theory normally used to describe the MAS NMR experiments is not only a mathematical description of the periodically time-dependent spin system, but can be interpreted as a differential rotation representation of the MAS NMR within a single set of renormalized states $|n\rangle$. The special form of the Hamiltonian allows us to consider sample rotation as a continuous spatial 'irradiation' in real space, which paves the way for the development of refined methods to evaluate MAS propagators in multi-spin systems, possibly with the help of Green's functions.

The time independent Floquet Hamiltonian in equation (47) is the same as the Floquet Hamiltonian derived from Shirley's theory. The Floquet operators $\hat{N}$ and $(\hat{X}_n, \hat{Y}_n, \hat{Z}_n)$ introduced by Zax *et al.* [15] to present the Floquet Hamiltonian are in fact related to the orbital angular momentum operators $\hat{R}_{z'}$ and the Floquet operators $(\hat{G}_{nx}, \hat{G}_{ny}, \hat{G}_{nz})$. Levante *et al.* [16] introduced the diagonal frequency displacement operator $\hat{W}^{\mathcal{F}}$, which is the additional term in the Floquet Hamiltonian reflecting the time-periodicity of the spin Hamiltonian. The physical interpretation of the diagonal frequency displacement operator in the case of MAS NMR spectroscopy is that part of the Hamiltonian associated with the sample spinning

$$\hat{\mathcal{H}}_R^{\mathcal{F}} = \omega_r \hat{N} = \omega_r \hat{R}_{z'}.$$

In section 6 the Floquet density operator was introduced according to the definition of Levante *et al.* and Weintraub and Vega [14]. Their definitions are not equivalent, since only the second one has a band structure. This difference leads to a different way of calcu-

lating expectation values of spin space operators. Although the definitions of the Floquet density operators are not the same, in both cases only the time-evolution of the Floquet evolution operator $U^{\mathcal{F}}(t) = \exp\{-i\hat{\mathcal{H}}^{\mathcal{F}}t\}$ must be calculated to obtain the expectation values. Thus with any of the two expressions for the expectation values the Floquet approach can be used to predict and simulate results of MAS NMR experiments.

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Appendix

In this article the magic angle spinning is described semi-classically, with the interaction between the classical macroscopic sample rotation and the quantum mechanical microscopic spin system included in the spin Hamiltonian. The interaction is expressed in terms of an infinitesimal spatial rotation operator $\hat{R}_{z'}$, and the Fourier operator $\hat{F}_n$. In this appendix it will be shown that both $\hat{R}_{z'}$ and $\hat{F}_n$ can be obtained from a quasi-classical Bohr-Sommerfeld quantization of the orbital angular momentum associated with the macroscopic rotation of an object around a fixed z' axis.

In quantum mechanics the components of the orbital angular momentum of an object are defined by the expectation values of orbital angular momentum operators $\hat{L}_x, \hat{L}_y$, and $\hat{L}_z$. These operators can be defined by their matrix elements in the representation of the eigenfunctions $|lm\rangle$ of $\hat{L}_z$ and $\hat{L}^2$, according to

$$\begin{aligned}\hat{L}_z|lm\rangle &= m|lm\rangle, \\ \hat{L}^2|lm\rangle &= l(l+1)|lm\rangle,\end{aligned}\quad (\text{A1})$$

and are given in units of $\hbar$. The spatial representation of the orbital angular momentum operator $\hat{L}_{z'}$ is $-i(\partial/\partial\varphi')$ and the spatial representation of the eigenstates $|lm\rangle$ are the spherical harmonics $Y_{lm}(\vartheta', \varphi')$, which are proportional to $P_l^{|m|}(\cos\vartheta')\exp(im\varphi')$ [28]. The classical limit for an object rotating around a fixed z' axis corresponds to $l \rightarrow \infty$, with $l = m$ and $\vartheta' = \pi/2$ [37]. During this quasi-classical motion $\hat{L}_{z'}$ is the relevant orbital angular momentum operator, with eigenvalues l , and quantum states $|ll\rangle \equiv |l\rangle$, which in the spatial representation is equal to $(2\pi)^{1/2}\exp(il\varphi')$.

This formalism can be used to generate a quantized representation of sample rotation. The rotation interacts with the spin system via a 'rotor field' which fluctuates periodically with only the spinning frequency ω_r .

Obviously the rotor field is a vector field which is fixed in space with a unique sense of rotation. This implies that the quasi-particle associated with this field has integral angular momentum 1 [38]. For this we can construct a boson quantized field:

$$\begin{aligned}\hat{a}|l\rangle &= l^{1/2}|l-1\rangle, \\ \hat{a}^\dagger|l\rangle &= (l+1)^{1/2}|l+1\rangle, \\ \hat{N}|l\rangle &= l|l\rangle,\end{aligned}\quad (\text{A } 2)$$

in which $\hat{a}, \hat{a}^\dagger$ are the well known boson annihilation and creation operators. The number operator is defined according to

$$\hat{N} = \hat{a}^\dagger \hat{a}, \quad (\text{A } 3)$$

and the commutation relations between those operators are

$$\begin{aligned}[\hat{a}, \hat{a}^\dagger] &= 1, \\ [\hat{N}, \hat{a}^\dagger] &= \hat{a}^\dagger, \\ [\hat{N}, \hat{a}] &= -\hat{a}.\end{aligned}\quad (\text{A } 4)$$

From equations (A 1) and (A 2) it follows immediately that

$$\hat{L}_{z'} = \hat{N}. \quad (\text{A } 5)$$

The total orbital angular momentum is thus proportional to the number of quasi-particles describing the rotating object. The energy of this system is equal to $\omega_r \hat{N}$ and the Hamiltonian defining the system therefore has the form

$$\hat{\mathcal{H}}_L^Q = \omega_r \hat{L}_{z'}, \quad (\text{A } 6)$$

according to equation (A 5). Using equation (A 2) the states $|l\rangle$ can be constructed from the ground state $|0\rangle$ according to

$$|l\rangle = \frac{(\hat{a}^\dagger)^l}{(l!)^{1/2}} |0\rangle. \quad (\text{A } 7)$$

In the quasi-classical limit $|l| \rightarrow \infty$. We can follow the procedure already indicated by Shirley [9] when we define $l = n + N$, in which $|N| \gg |n|$ is the number of quasi-particles in the rotor 'bath' and n represents the variation associated with the interaction of the rotor bath with the spin system. In the quasi-classical limit the approximations $|N| \rightarrow \infty$, and $N + n \approx N$ are used, yielding

$$\begin{aligned}|n + N\rangle &= \frac{(\hat{a}^\dagger)^{n+N}}{[(n+N)!]^{1/2}} |0\rangle \\ &\approx \left(\frac{\hat{a}^\dagger}{N^{1/2}}\right)^n |N\rangle\end{aligned}\quad (\text{A } 8)$$

and

$$\begin{aligned}| -n + N\rangle &= \frac{(\hat{a}^\dagger)^{-n+N}}{[(-n+N)!]^{1/2}} |0\rangle \\ &\approx \left(\frac{\hat{a}}{N^{1/2}}\right)^n |N\rangle.\end{aligned}\quad (\text{A } 9)$$

We can now define the scaled creation and annihilation operators

$$\begin{aligned}\hat{a}_n &= \left(\frac{\hat{a}^\dagger}{N^{1/2}}\right)^n, \\ \hat{a}_{-n} &= \left(\frac{\hat{a}}{N^{1/2}}\right)^n,\end{aligned}\quad (\text{A } 10)$$

with $\hat{a}_0$ the unity operator. From equations (A 4) and (A 5) the commutation relations between $\hat{L}_{z'}$ and $\hat{a}_n$ can be derived

$$\begin{aligned}[\hat{L}_{z'}, \hat{a}_n] &= \left[\hat{N}, \left(\frac{\hat{a}^\dagger}{N^{1/2}}\right)^n\right] \\ &= n \left(\frac{\hat{a}^\dagger}{N^{1/2}}\right)^n + \left(\frac{\hat{a}^\dagger}{N^{1/2}}\right)^n \hat{N} - \left(\frac{\hat{a}^\dagger}{N^{1/2}}\right)^n \hat{N} \\ &= n \hat{a}_n.\end{aligned}\quad (\text{A } 11)$$

The scaled creation and annihilation operators $\hat{a}_n$ can be considered as raising and lowering operators

$$\begin{aligned}\hat{a}_k |n + N\rangle &= \hat{a}_k \hat{a}_n |N\rangle \\ &= |n + k + N\rangle,\end{aligned}\quad (\text{A } 12)$$

and the spatial representation of $\hat{a}_k$ becomes $\exp(ik\varphi')$.

In this framework the total Hamiltonian of the spin system interacting with a quantized rotor field is [9]

$$\hat{\mathcal{H}}^Q = \hat{\mathcal{H}}_Z^Q + \hat{\mathcal{H}}_i^Q + \hat{\mathcal{H}}_L^Q. \quad (\text{A } 13)$$

in which $\hat{\mathcal{H}}_Z^Q$ is the Zeeman Hamiltonian, $\hat{\mathcal{H}}_L^Q$ the rotor Hamiltonian, given in equation (A 6) and $\hat{\mathcal{H}}_i^Q$ describes the interaction of the spin system with the rotor using the scaled creation and annihilation operators. This Hamiltonian can be used to provide a quantized description of the MAS NMR. However, the energy associated with the sample rotation is very large if $|N| \rightarrow \infty$, while only the interaction between the sample rotation and the spin system is observable in a NMR experiment. For this reason we renormalize

the Hamiltonian in equation (A 13), by subtracting a constant energy $\omega_R N$, in frequency units, yielding

$$\hat{\mathcal{H}}'^Q = \hat{\mathcal{H}}_S^Q + \omega_r \hat{L}_{z'}'. \quad (\text{A } 14)$$

Here we have introduced a renormalized orbital angular momentum operator, according to

$$\hat{L}_{z'}' = \hat{L}_{z'} - N\hat{a}_0. \quad (\text{A } 15)$$

The spin Hamiltonian $\hat{\mathcal{H}}_S^Q$ is the sum of the Zeeman term and the interaction term. It should be emphasized that the renormalization of the angular momentum operator only affects the energy and will not influence any spin observation.

The renormalized operator $\hat{L}_{z'}'$ can be used to measure the variation n relative to the background N in the state $|n + N\rangle$, since both $\hat{L}_{z'}'$ and the quantum states $|N + n\rangle$ depend linearly on N . Therefore the matrix elements

$$\langle m + N | \hat{L}_{z'}' | n + N \rangle = n\delta_{nm} \quad (\text{A } 16)$$

are independent of N . It is then possible to identify the interaction between rotor bath and spin system in the state $|N + n\rangle$ with a differential rotation n relative to N , with n the eigenvalues of the renormalized orbital angular momentum, since

$$\hat{L}_{z'}' |N + n\rangle = n |N + n\rangle. \quad (\text{A } 17)$$

However, since the matrix elements

$$\langle m + N | \hat{a}_k | n + N \rangle = \delta_{m(n+k)}. \quad (\text{A } 18)$$

are also independent of N , only this differential rotation is in fact important for the description of the MAS. This leads to a projection of the interaction onto a single set of renormalized states $|n\rangle$, with n the eigenvalues of the orbital angular momentum, according to

$$L_{z'}' |n\rangle = n |n\rangle. \quad (\text{A } 19)$$

The states $|n\rangle$ are the equivalent of the Fourier states in our semi-classical approach. The spatial representations of these states are $(2\pi)^{-1/2} \exp(in\varphi')$.

The analogy between equation (A 19) and equation (1) illustrates that $\hat{R}_{z'}'$ corresponds to the orbital angular momentum operator, $\hat{L}_{z'}'$. In addition, the spatial representation of $\hat{R}_{z'}'$ is $-i(\partial/\partial\varphi')$, which is identical to the spatial representation of the orbital angular momentum operator $\hat{L}_{z'}'$, and the spatial representation of $\hat{F}_k$ is $\exp(ik\varphi')$, which is identical to the spatial representation of $\hat{a}_k$. The equivalents of the matrix elements given in equation (A 16) and (A 18) are

$$\langle m | \hat{R}_{z'}' | n \rangle = n\delta_{nm} \quad (\text{A } 20)$$

and

$$\langle m | \hat{F}_k | n \rangle = \delta_{m(n+k)}, \quad (\text{A } 21)$$

independent of N .

In fact it is in the quasi-classical formalism that the renormalization of the operators $L_{z'}' \rightarrow L_{z'}''$ is replaced by a renormalization of the states $|N + n\rangle \rightarrow |n\rangle$. This step formally requires $N \rightarrow 0$, which can be done without loss of generality provided the $\hat{a}_n$ are defined independently for $|N| \rightarrow \infty$, since the matrix elements $\langle m + N | \hat{a}_k | n + N \rangle$ are independent of N , according to equation (A 18). Likewise, in the semi-classical Floquet description the matrix elements $\langle m + N | \hat{F}_k | n + N \rangle$ are independent of N , but the introduction of two degrees of freedom in equation (29) is essential. First, the φ' leads to the correct $\hat{F}_n$ with $\Delta\varphi' = 0$. In parallel a complete representation of the MAS within the single set of renormalized states $|n\rangle$ can be obtained along the second degree of freedom t . The spatial representation of the Floquet Hamiltonian

$$\hat{\mathcal{H}}^{\mathcal{F}} = \hat{\mathcal{H}}_S^{\mathcal{F}} + \omega_r \hat{R}_{z'}', \quad (\text{A } 22)$$

describing the renormalized energy, is identical to the spatial representation of $\hat{\mathcal{H}}^Q$, while the matrix elements of the renormalized Hamiltonian $\hat{\mathcal{H}}'^Q$ are

$$\langle m + N | \hat{\mathcal{H}}'^Q | n + N \rangle = \langle m | \hat{\mathcal{H}}^{\mathcal{F}} | n \rangle. \quad (\text{A } 23)$$

In this framework there is

$$[\hat{R}_{z'}', \hat{F}_n] = n\hat{F}_n, \quad (\text{A } 24)$$

isomorphic with equation (A 11). Those equations imply that in both cases the transformation under sample rotation of the Hamiltonian, e.g. from the rotor angle frame to the rotor frame, are independent of N , since $\hat{\mathcal{H}}^Q$ is expressed in terms of $\hat{a}_n$, and $\hat{\mathcal{H}}^{\mathcal{F}}$ is expressed in terms of $\hat{F}_n$.

It is thus possible to describe sample spinning in a N independent approach using Floquet Hamiltonian $\hat{H}^{\mathcal{F}}$ and a single set of Fourier states $|n\rangle$, leading to the semi-classical approach given in this article.

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