Operator-based triple-mode Floquet theory in solid-state NMR

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Many solid-state NMR experiments exploit interference effects between time dependencies in the system Hamiltonian to design an effective time-independent Hamiltonian with the desired properties. Effective Hamiltonians can be designed such that they contain only selected parts of the full system Hamiltonian while all other parts are averaged to zero. A general theoretical description of such experiments has to accommodate several time-dependent perturbations with incommensurate frequencies. We describe an extension of the analytical operator-based Floquet description of NMR experiments to situations with three incommensurate frequencies. Experiments with three time dependencies are quite common in solid-state NMR. Examples include experiments which combine magic-angle spinning and radio-frequency irradiation on two nuclei or asynchronous multiple-pulse sequences on a single spin species. The Floquet description is general in the sense that the resulting effective Hamiltonians can be calculated without a detailed knowledge of the spin-system Hamiltonian and can be expressed fully as a function of the Fourier components of the time-dependent Hamiltonian. As a prototype experiment we treat the application of two continuous-wave (cw) radio-frequency fields under magic-angle spinning. Experiments that are included in such a description are Hartmann-Hahn cross polarization or rotary-resonance recoupling experiments with simultaneous cw decoupling. © 2007 American Institute of Physics. [DOI: 10.1063/1.2800319]

I. INTRODUCTION

Pulse sequences that result in effective Hamiltonians where only certain parts of the full system Hamiltonian are retained while all other interactions are averaged to zero form the basis of many solid-state NMR experiments. Such sequences often rely on interference effects between different time dependencies of the Hamiltonian. The time dependencies are generated by magic-angle spinning or by application of rf irradiation during certain parts of the experiment and lead to a modulation of the spatial and spin parts of the Hamiltonian, respectively.\(^1\)\(^-\)\(^3\) Therefore, methods to describe the time evolution of spin systems under time-dependent Hamiltonians play an important role among the tools used to analyze solid-state NMR experiments.

Average-Hamiltonian theory\(^3\) (AHT) is a commonly used technique to obtain a series expansion of an approximate time-averaged Hamiltonian for a system with a single time dependence or multiple commensurate time dependencies. Typical examples of experiments that can be treated by AHT are rotor-synchronized pulse sequences\(^4,5\) for the recoupling of anisotropic interactions under magic-angle spinning (MAS) or homonuclear multiple-pulse decoupling sequences in static samples.\(^1\) Another approach to describe time-dependent Hamiltonians is Floquet theory\(^5,7\) where the finite-dimensional time-dependent Hilbert-space Hamiltonian is transformed into an infinite-dimensional time-independent Floquet-space Hamiltonian that contains the equivalent information. So far, Floquet theory has been applied to problems in solid-state NMR with one or two incommensurate frequencies\(^4,8\) using mostly matrix-based perturbation methods or numerical calculations.

Combining an operator-based formulation of the Floquet Hamiltonian\(^9,16\) with the operator-based van Vleck–Primas perturbation method\(^11-\)\(^14\) allows the calculation of an effective analytical Hamiltonian in the spin-Hilbert space.\(^15-\)\(^18\) In this formulation, Floquet theory can be seen as a generalization of AHT for multiple incommensurate time dependencies. Such an effective Hamiltonian formulation of Floquet theory has been developed for the case of one and two frequencies. In this publication we extend the effective Hamiltonian treatment to three independent frequencies.

There are quite a number of examples where a bimodal Floquet treatment is required for the analysis of solid-state NMR experiments. The first example is double rotation\(^19\) (DOR) in order to obtain high-resolution spectra of quadrupolar nuclei.\(^8\) In this case, the two frequencies for the bimodal Floquet treatment are the two spinning frequencies of the inner and outer rotors. A second area is the combination of cyclic pulse sequences and sample rotation (in particular, MAS) in a way that the pulse sequence and the sample rotation are not synchronized. Such a situation can be found in homonuclear decoupling under MAS using frequency-switched\(^20,21\) or phase-modulated\(^15,16\) Lee-Goldburg irradiation. Other sequences are cyclic nonsynchronized heteronuclear decoupling sequences such as continuous-wave\(^18,22\) (cw) or XiX decoupling\(^23\) which can...
also be characterized using two incommensurate frequencies. In all these pulse sequences, the two frequencies are given by the rotor frequency of the MAS and the basic Fourier frequency of the pulse sequence which is obtained in an interaction-frame transformation that eliminates the rf field from the system Hamiltonian.

There are also many examples of pulse sequences where three frequencies are needed to characterize the Hamiltonian. In such a case a trimodal Floquet Hamiltonian is required if the three frequencies are incommensurate. An example for a pulse sequence with three incommensurate frequencies is simultaneous cw irradiation of two nuclei under MAS. Examples for this situation are cross polarization (CP) under MAS and cw recoupling experiments such as rotary resonance or HORROR (Refs. 27 and 28) with simultaneous cw decoupling on the protons. Other examples for pulse sequences which require a trimodal Floquet approach are cw irradiation under DOR, asynchronous phase-modulated decoupling sequences such as two-pulse phase-modulated (TPPM) decoupling and its variants, or cw decoupling while simultaneously recoupling using a rotor-synchronized multiple-pulse sequence.

The description of experiments using multimode Floquet theory can be simplified on the resonance conditions where two or more of the frequencies can be expressed as a multiple of a common basic frequency. In such cases, the multimode Floquet representation can be projected onto a lower-dimensional Floquet space. There is, however, no requirement to carry out this projection because the problem can be solved in the full Floquet space. The advantage of a multimode Floquet approach to the effective Hamiltonian is that all resonance conditions and the nonresonant terms can be described within a single theoretical framework. In contrast, average Hamiltonian theory requires a separate ansatz for every single resonance condition and is not applicable to the nonresonant case.

In this contribution we will extend the van Vleck–Floquet formalism to situations with three incommensurate frequencies and derive the effective Hamiltonians in this situation for resonant and nonresonant conditions. The general results can be applied to any problem with three frequencies since it does not depend on the detailed structure of the Hilbert-space Hamiltonian but only on the Fourier spaces of the Floquet Hamiltonian. We will illustrate the results of the general theory using the example of simultaneous cw irradiation of two spin species under MAS to show the validity of this approach in special cases where the results are well known.

II. GENERAL THEORY

We start with the full time-dependent Hilbert-space Hamiltonian which can be written as an infinite Fourier series modulated by three characteristic frequencies

\[ \hat{H}(t) = \sum_{n=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \hat{H}^{(n,k,\ell)}(t) e^{in\omega_r t} e^{ik\omega_m t} e^{i\ell\omega_p t}, \]

with the Fourier components of the Hamiltonian given by \( \hat{H}^{(n,k,\ell)}(t) \) and the three characteristic frequencies being \( \omega_r \), \( \omega_m \), and \( \omega_p \). Starting from such a formulation of the time-dependent finite-dimensional Hamiltonian, we can construct the equivalent time-independent but infinite-dimensional Floquet Hamiltonian

\[ \hat{H}_F = \omega_r \hat{F}_r + \omega_m \hat{F}_m + \omega_p \hat{F}_p + \sum_{n=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \hat{H}^{(n,k,\ell)} \otimes \hat{F}_r \otimes \hat{F}_m \otimes \hat{F}_p. \]

In order to apply perturbation theory, we split the full Hamiltonian into a diagonal part

\[ \hat{H}_F^{(1)} = \omega_r \hat{F}_r + \omega_m \hat{F}_m + \omega_p \hat{F}_p \]

and a perturbative part

\[ \hat{H}_F^{(1)} = \sum_{n=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \hat{H}^{(n,k,\ell)} \otimes \hat{F}_r \otimes \hat{F}_m \otimes \hat{F}_p. \]

that contains all the detailed information about the spin physics of the problem. The Fourier operators are defined by

\[ \hat{F}_n |m\rangle = m |m\rangle, \]

\[ \hat{F}_n |m\rangle = |n + m\rangle, \]

where \( m \) and \( n \) are integers. The commutation relations

\[ [\hat{F}_m, \hat{F}_n] = m \hat{F}_m, \]

\[ [\hat{F}_m, \hat{F}_n] = 0 \]

and the multiplication rule

\[ \hat{F}_m \hat{F}_n = \hat{F}_{m+n} \]

are also fulfilled. The matrix elements of the Fourier operators are given by

\[ \langle m_1 | \hat{F}_n | m_2 \rangle = \begin{cases} 0, & m_1 - m_2 \neq n \\ 1, & m_1 - m_2 = n \end{cases} \]

(8)

and

\[ \langle m_1 | \hat{F}_m | m_2 \rangle = \begin{cases} 0, & m_1 \neq m_2 \\ 1, & m_1 = m_2 \end{cases} \]

(9)

In order to block diagonalize the full Floquet Hamiltonian, we have to find a unitary transformation

\[ \hat{A}_F = \hat{U} \hat{H}_F \hat{U}^\dagger = \hat{H}_F^{(0)} + \hat{W}_F \]

(10)

that fulfills the commutation rules \( [\hat{H}_F^{(0)}, \hat{A}_F] = 0 \) and \( [\hat{H}_F^{(0)}, \hat{W}_F] = 0 \). We can express the propagator as an exponential operator \( \hat{U} = e^{\hat{S}} \) and expand \( \hat{A}_F \) and \( \hat{S} \) in the framework of perturbation theory as.
The different orders of $\hat{H}_F^{(q)}$ and $\hat{S}^{(q)}$ can be calculated using the Baker-Campbell-Hausdorff expansion for a general trinodal Floquet Hamiltonian in full analogy to the solutions for bimodal Floquet problems.\(^{2,13,18}\) The first three orders of the expansion of the operator $\hat{\Lambda}_F$ are given by

\[
\hat{\Lambda}_F^{(1)} = \sum_{n_0, k_0, \ell_0} \hat{h}^{(n_0, k_0, \ell_0)} \hat{F}^{m}_{n_0} \hat{F}^{p}_{k_0} \hat{\ell}_0,
\]

\[
\hat{\Lambda}_F^{(2)} = \frac{1}{2} \sum_{n_0, k_0, \ell_0} \sum_{v, \kappa, \lambda} \frac{[\hat{h}^{(n_0, v, k_0, \kappa, \ell_0, \lambda)}, \hat{h}^{(v, \kappa, \lambda)}] \hat{F}^{m}_{n_0} \hat{F}^{p}_{k_0} \hat{\ell}_0}{(v \omega_r + \kappa \omega_m + \lambda \omega_p)(v' \omega_r + \kappa' \omega_m + \lambda' \omega_p)},
\]

\[
\hat{\Lambda}_F^{(3)} = \frac{1}{3} \sum_{n_0, k_0, \ell_0} \sum_{v, \kappa, \lambda, v', \kappa', \lambda'} \frac{[\hat{h}^{(n_0, v, k_0, \kappa, \ell_0, \lambda)}, \hat{h}^{(v, \kappa, \lambda)}] \hat{F}^{m}_{n_0} \hat{F}^{p}_{k_0} \hat{\ell}_0}{(v \omega_r + \kappa \omega_m + \lambda \omega_p)^2}.
\]

For Eqs. (13) and (14) the general conditions $n_0 \omega_r + k_0 \omega_m + \ell_0 \omega_p = 0$, $n_0 \omega_r + k_0 \omega_m + \ell_0 \omega_p = 0$, and $n_0 \omega_r + k_0 \omega_m + \ell_0 \omega_p = 0$ have to be fulfilled. Throughout this paper we will use the following convention: $n, k,$ and $\ell$ will always sum over all possible values of the three indices, $n_0, k_0,$ and $\ell_0$ will only sum over the values for which the condition $n_0 \omega_r + k_0 \omega_m + \ell_0 \omega_p = 0$ is fulfilled, while $v, \kappa,$ and $\lambda$ will only sum over the values for which the condition $v \omega_r + \kappa \omega_m + \lambda \omega_p = 0$ is fulfilled. Note that in Eq. (14) the variables have to be further restricted to values $(v + v') \omega_r + (\kappa + \kappa') \omega_m + (\lambda + \lambda') \omega_p = 0$ for the first summation and to values $(v + v') \omega_r + (\kappa + \kappa') \omega_m + (\lambda + \lambda') \omega_p = 0$ for the second summation.

The first two terms of the operators $\hat{S}^{(0)}$ are given by

\[
\hat{S}^{(1)} = -\sum_{v, \kappa, \lambda} \frac{\hat{h}^{(v, \kappa, \lambda)} \hat{F}^{m}_{v} \hat{F}^{p}_{\kappa} \hat{\ell}_{\lambda}}{v \omega_r + \kappa \omega_m + \lambda \omega_p},
\]

and

\[
\hat{S}^{(2)} = \frac{1}{2} \sum_{v, \kappa, \lambda, v', \kappa', \lambda'} \frac{[\hat{h}^{(v, \kappa, \lambda)} \hat{h}^{(v', \kappa', \lambda')} \hat{F}^{m}_{v} \hat{F}^{p}_{\kappa} \hat{\ell}_{\lambda}}{(v' \omega_r + \kappa' \omega_m + \lambda' \omega_p)((v + v') \omega_r + (\kappa + \kappa') \omega_m + (\lambda + \lambda') \omega_p)}
\]

\[
+ \sum_{v, \kappa, \lambda, n_0, k_0, \ell_0} \frac{[\hat{h}^{(n_0, v, k_0, \kappa, \ell_0, \lambda)} \hat{h}^{(n_0, v', k_0, \kappa', \ell_0, \lambda')}] \hat{F}^{m}_{n_0} \hat{F}^{p}_{k_0} \hat{\ell}_{\ell_0}}{(v \omega_r + \kappa \omega_m + \lambda \omega_p)^2}.
\]

Here, the conditions $n_0 \omega_r + k_0 \omega_m + \ell_0 \omega_p = 0$, $n_0 \omega_r + k_0 \omega_m + \ell_0 \omega_p = 0$, and $(v + v') \omega_r + (\kappa + \kappa') \omega_m + (\lambda + \lambda') \omega_p = 0$ have to be fulfilled. The expressions of Eqs. (12)–(14) for the operators $\hat{\Lambda}_F^{(q)}$ can now be used to calculate the perturbation expansion of $\hat{H}_F$ if the Fourier coefficients, $\hat{h}^{(n, k, \ell)}$, of a problem are known.

In order to calculate an effective spin-Hilbert-space Hamiltonian, we project the approximately diagonalized Floquet Hamiltonian back into Hilbert space. The effective Hamiltonian is given by

![FIG. 1. Pulse sequence for the basic experiment that will be used to illustrate and validate the results of the trinodal Floquet treatment. In an $S_3$-three-spin system, an initial density operator $\rho_0=S_{1s}$ is generated by a selective pulse. The density operator then evolves for the time $\tau_m$ under the rf fields with amplitudes $\omega_{1s}$ and $\omega_{2s}$. At the end, the expectation values $\langle \hat{I}_1 \rangle$, $\langle \hat{S}_{1s} \rangle$, and $\langle \hat{S}_{2s} \rangle$ are detected.](image-url)
\[
\tilde{\mathcal{H}} = \sum_{n} \sum_{k'} \sum_{\ell'} \langle n, k, \ell | \tilde{\mathcal{H}}^{(0)} \rangle + \tilde{\mathcal{H}}^{(1)} + \tilde{\mathcal{H}}^{(2)} + \cdots \langle n + n', k + k', \ell + \ell' | \tilde{\mathcal{H}} \rangle
\]

leading to

\[
\tilde{\mathcal{H}} = \sum_{n} \tilde{\mathcal{H}}^{(0)} + \sum_{n} \tilde{\mathcal{H}}^{(1)} + \sum_{n} \tilde{\mathcal{H}}^{(2)} + \cdots
\]

with

\[
\tilde{\mathcal{H}}^{(2)} = -\frac{1}{2} \sum_{n,k,\lambda} \left[ \tilde{\mathcal{H}}^{(0)}(n-k,\lambda) \tilde{\mathcal{H}}^{(r,\lambda,\lambda)}(n,\lambda) / (\nu \omega_r + \kappa \omega_m + \lambda \omega_p) \right]
\]

and

\[
\tilde{\mathcal{H}}^{(3)} = \frac{1}{3} \sum_{n,k,\lambda} \sum_{n',k',\lambda'} \left[ \tilde{\mathcal{H}}^{(0)}(n-k,\lambda) \tilde{\mathcal{H}}^{(r,\lambda,\lambda')} / (\nu \omega_r + \kappa \omega_m + \lambda \omega_p) \right]
\]

\[
+ \frac{1}{2} \sum_{n,k,\lambda} \sum_{n',k',\lambda'} \left[ \tilde{\mathcal{H}}^{(0)}(n-k,\lambda) \tilde{\mathcal{H}}^{(r,\lambda',\lambda')} / (\nu \omega_r + \kappa \omega_m + \lambda \omega_p)^2 \right].
\]
Note that in Eq. (20) the sums have to be again further restricted to values \((v + v')\omega_n + (\kappa + \kappa')\omega_m + (\lambda + \lambda')\omega_p \neq 0\) for the first summation and to values \((v + v')\omega_n + (\kappa + \kappa')\omega_m + (\lambda + \lambda')\omega_p = 0\) for the second summation.

Equations (18)–(20) form the central result of this publication. They can be used to calculate the effective Hamiltonian for resonant and nonresonant conditions. The resonance condition is defined by

\[ n_0\omega_r + k_0\omega_m + \ell_0\omega_p = 0 \tag{21} \]

and determines which of the terms \(\hat{H}_{(i)}^{(m,n,k,p)}\) are important in the effective Hamiltonian of Eq. (18). This is the only change in the formalism when describing experiments at different resonance conditions. In the case of nonresonant experiments, only the terms \(\hat{H}_{(i)}^{(0,0,0)}\) are important.

### III. APPLICATION TO SIMULTANEOUS CW IRRADIATION OF TWO SPIN SPECIES UNDER MAS

Simultaneous cw rf irradiation on two different spin species, \(I\) and \(S\), under MAS describes a situation that is realized in a number of experiments such as cross polarization\(^{24}\) or cw recoupling experiments on the \(S\) spins such as rotary-resonance\(^{25,26}\) or HORROR (Refs. 27 and 28) recoupling with simultaneous cw decoupling on the \(I\) spins. Figure 1 shows schematically the experiment that was simulated to illustrate the features of simultaneous cw irradiation on an \(I_2S_2\) three-spin system. After a selective pulse on the spin \(S_1\), the spin-locked magnetization can evolve under the influence of the two rf fields with amplitudes \(\omega_{I,S}\) and \(\omega_{I}\). Starting from an initial density operator \(\rho_0=S_{1z}\), the time evolution under the full time-dependent Hamiltonian was numerically calculated using the GAMMA spin simulation environment.\(^{30}\) Figure 2 shows the expectation values \(\langle S_{1z} \rangle\) [Fig. 2(a)], \(\langle I \rangle\) [Fig. 2(b)], and \(\langle S_{2z} \rangle\) [Fig. 2(c)] after a time evolution of 10 ms to allow transient oscillations to dampen out. The two rf-field amplitudes \(\omega_{I,S}\) and \(\omega_{I}\) were varied in a range from 0 to 180 kHz at a MAS frequency of \(\omega_r/(2\pi) = 20\text{ kHz}\).

One can clearly see the \(n=\pm 1, \pm 2\) Hartmann-Hahn conditions that allow cross polarization to the \(I\) spin. They correspond to the resonance conditions \(n\omega_r = \omega_{I,S} - \omega_{I}\) and are manifest as strong bands parallel to the diagonal in Figs. 2(a) and 2(b). In addition, the \(n=0\) and the higher-order \(n=\pm 3, \pm 4\) Hartmann-Hahn conditions are also visible as narrow bands parallel to the diagonal. The HORROR and the rotary-resonance conditions are visible as light horizontal bands [Fig. 2(a)] at \(\omega_{I,S}/(2\pi) = 10, 20, 40, 60, \) and 80 kHz because of a line broadening due to recoupling at these conditions. These effects can also be seen in Figs. 2(d)–2(f) which shows slices through the two-dimensional (2D) plots of Fig. 2 along the antidiagonal, while Figs. 2(g)–2(i) show slices through the 2D plots parallel to the \(\omega_{I,S}\) axis at \(\omega_{I}/(2\pi) = 150\text{ kHz}\). One can clearly see the broad \(n=\pm 1, \pm 2\), the narrow \(n=0\), and the narrow \(n=\pm 3, \pm 4\) Hartmann-Hahn conditions. One can also see the strong HORROR and, \(n=1,2\) rotary-resonance conditions at \(\omega_{I,S}/(2\pi) = 10, 20, \) and 40 kHz, respectively [Fig. 2(g)]. The much weaker \(n=3,4\) rotary-resonance conditions are visible at \(\omega_{I,S}/(2\pi) = 60\) and 80 kHz. There is also a broad band parallel to the diagonal near the \(n=0\) Hartmann-Hahn condition which is best visible in Fig. 2(c), corresponding to the homonuclear third-spin assisted recoupling (TSAR) experiment,\(^{31}\) where the polarization transfer is mediated by the nonresonant terms as discussed later in this paper.

The Hamiltonian of a heteronuclear spin system with \(N_I\) \(I\) spins and \(N_S\) \(S\) spins in a coordinate system rotating with the two Larmor frequencies is given by

\[
\hat{H}(t) = \sum_{n=1}^{N_S} \sum_{m=1}^{N_I} \omega^{(n)}_{p}\hat{S}_{pc}^{(n)}\hat{S}_{pc}^{(n)} + \sum_{m=1}^{N_I} \omega^{(m)}_{p}\hat{I}_{mc}^{(m)}\hat{I}_{mc}^{(m)} + \sum_{n=1}^{N_S} \sum_{m=1}^{N_I} \sum_{n=1}^{N_S} \omega^{(n)}_{S_p}\hat{S}_{pc}^{(n)}\hat{S}_{pc}^{(n)}(2I_{\ell}\hat{J}_{mc} - (I_{\ell}\hat{I}_{mc} + \hat{I}_{mc}\hat{I}_{mc})) + \sum_{\ell < m}^{N_I} \omega^{(0)}_{I,\ell,m}\hat{I}_{\ell}\hat{I}_{m} + \sum_{p < q}^{N_S} \sum_{n=1}^{N_S} \omega^{(n)}_{S_p} S_{pc}^{(n)} - (S_{p1}S_{q1} + S_{p2}S_{q2})\hat{S}_{pq}\hat{S}_{pq} + \sum_{p < q}^{N_S} \sum_{n=1}^{N_S} \sum_{m=1}^{N_I} \omega^{(n)}_{S_p} \hat{S}_{pq}^{(n)}\hat{S}_{pq}^{(n)} + \omega_{I_S}\sum_{m=1}^{N_I} \hat{I}_{mc}^{(m)} + \omega_{I}\sum_{m=1}^{N_I} \hat{I}_{mc}^{(m)}.
\tag{22}
\]

This experiment has in the general case three different characteristic frequencies: (i) the MAS frequency \(\omega_r\), (ii) the cw rf-field amplitude on the \(I\) spins \(\omega_{I}\), and (iii) the cw rf-field amplitude on the \(S\) spins \(\omega_{I,S}\). The constants \(\omega^{(n)}_{S_p}\) and \(\omega^{(n)}_{I_m}\) are the Fourier coefficients of the chemical-shift (CSA) tensor under MAS of spins \(S_p\) and \(I_m\), respectively. The constants \(\omega^{(n)}_{p}\) and \(\omega^{(n)}_{q}\) are the Fourier coefficients of the heteronuclear and homonuclear dipolar coupling tensors under MAS. The terms with \(n=0\) describe the isotropic \(J\) couplings. Detailed expressions for these terms can be found in the Appendix. We transform the Hamiltonian of Eq. (22) into a tilted frame rotating with the two rf-field amplitudes with the \(z\) axis along the direction of the rf fields. The interaction-frame Hamiltonian is then given by
From the time-dependent interaction-frame Hamiltonian of Eq. (23) the Fourier coefficients of the Hamiltonian can be identified as

\[ \hat{\mathcal{H}}^{(0,0,0)} = \sum_{\ell < m} \omega_{\ell m}^{(0)} \hat{I}_\ell \cdot \hat{I}_m + \sum_{p < q} \omega_{p q}^{(0)} \hat{S}_p \cdot \hat{S}_q, \]

\[ \hat{\mathcal{H}}^{(n,0,0)} = -\frac{1}{2} \sum_{\ell < m} \omega_{\ell m}^{(n)} [2I_{\ell m} - (I_{\ell x}I_{m x} + I_{\ell y}I_{m y})] \]

\[ -\frac{1}{2} \sum_{p < q} \omega_{p q}^{(n)} [2S_{p q}S_{q c} - (S_{p x}S_{q x} + S_{p y}S_{q y})], \]

\[ \hat{\mathcal{H}}^{(n,1,0)} = -\frac{1}{2} \sum_{m = 1}^{N_1} \omega_{m}^{(n)} I_m^2, \]

\[ \hat{\mathcal{H}}^{(n,0,1)} = -\frac{1}{2} \sum_{p = 1}^{N_2} \omega_{p}^{(n)} S_p^2, \]

\[ \hat{\mathcal{H}}^{(n,1,1)} = \frac{1}{2} \sum_{m = 1}^{N_1} \sum_{p = 1}^{N_2} \omega_{m p}^{(n)} S_m^x S_p^x, \]

\[ \hat{\mathcal{H}}^{(n,2,0)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell m}^{(n)} I_{\ell m}^2, \]

\[ \hat{\mathcal{H}}^{(n,0,2)} = \frac{3}{4} \sum_{p < q} \omega_{p q}^{(n)} S_p^2 S_q^2. \]

The values of \( n \) are limited to \(-2 < n < 2\) for all the terms in Eq. (24). In addition, \( n \neq 0 \) must be fulfilled for all the terms originating from the homonuclear dipolar couplings [\( \hat{\mathcal{H}}^{(n,0,0)} \), \( \hat{\mathcal{H}}^{(n,2,0)} \), and \( \hat{\mathcal{H}}^{(n,0,2)} \)]. The Fourier coefficients of the Hamiltonian with respect to the three basic frequencies \( \omega_r \), \( \omega_\ell \), and \( \omega_s \) [Eq. (24)] in combination with the general results of Eqs. (18)–(20) allow us to calculate the desired effective Hamiltonians for the cw irradiation experiments.

### A. First-order resonance conditions

The resonance conditions are characterized by the condition \( n_0 \omega_r + k_0 \omega_\ell + \ell_0 \omega_s = 0 \). For first-order resonance conditions, we only consider the Floquet blocks \( \hat{\mathcal{H}}^{(n_0,k_0,\ell_0)} \) which limits the allowed values \( n_0 = -2, -1, 0, 1, 2 \), \( k_0 = -2, -1, 0, 1, 2 \), and \( \ell_0 = -2, -1, 0, 1, 2 \). Each resonance condition is characterized by the triplet \( (n_0,k_0,\ell_0) \) and corresponds to a resonance condition given by \( k_0 \omega_1 + \ell_0 \omega_{15} = -n_0 \omega_r \). All possible resonance conditions that have nonzero Floquet blocks up to second order in the perturbation treatment can be found in Table I.

### 1. Hartmann-Hahn matching conditions

The Hartmann-Hahn matching conditions for CP are defined by the triplets \( (n_0,k_0,\ell_0) = (0, \pm 1, \mp 1) \) for the \( n = 0 \) Hartmann-Hahn condition, by \( (n_0,k_0,\ell_0) = (\pm 1, \pm 1, \mp 1) \) (zero-quantum CP) and \( (n_0,k_0,\ell_0) = (\pm 1, \pm 1, \pm 1) \) (double-quantum CP) for the \( n = 1 \) Hartmann-Hahn condition, and by \( (n_0,k_0,\ell_0) = (\pm 2, \pm 1, \mp 1) \) (zero-quantum CP) and \( (n_0,k_0,\ell_0) = (\pm 2, \pm 1, \pm 1) \) (double-quantum CP) for the \( n = 2 \) Hartmann-Hahn matching condition.

At the \( n = 0 \) Hartmann Hahn condition (\( \pm \omega_1 + \omega_{15} = 0 \)), the effective Hamiltonian for zero-quantum polarization transfer is given by

\[ \tilde{\mathcal{H}} = \tilde{\mathcal{H}}^{(0,0,0)} + \tilde{\mathcal{H}}^{(0,-1,1)} + \tilde{\mathcal{H}}^{(0,1,-1)} \]

\[ = \sum_{\ell < m} \omega_{\ell m}^{(0)} \hat{I}_\ell \cdot \hat{I}_m + \sum_{p < q} \omega_{p q}^{(0)} \hat{S}_p \cdot \hat{S}_q + \frac{1}{2} \sum_{\ell \neq m} \omega_{\ell m}^{(0)} \hat{I}_\ell \cdot \hat{S}_\ell + \hat{\Gamma}_\ell \hat{S}_\ell. \]
double-quantum polarization transfer, the zero-quantum flop terms of the heteronuclear dipolar couplings that promote the heteronuclear polarization transfer. In the case of double-quantum polarization transfer, the zero-quantum operators have to be replaced by double-quantum operators. The \( n = \pm 1, \pm 2 \) conditions can clearly be seen in Figs. 2(d) and 2(e) at \( (\omega_{1f} - \omega_{1S})/\omega_r = \pm 1 \) and \( \pm 2 \) as polarization transfer from \( S_I \) to the \( I \) spin.

The Hartmann-Hahn conditions can also be described using average Hamiltonian theory due to the fact that a single frequency, namely \( \omega_r \), can be used to describe the time dependence of the spin-system Hamiltonian. The Floquet results shown in Eqs. (25) and (26) agree with the results obtained by AHT. The Floquet-theory-based effective Hamiltonian formalism presented here has the advantage that all resonance conditions can be obtained in a single ansatz. The different resonance conditions are distinguished only in the selection of the Fourier coefficients that are important for the given experiment.

### Table I. Triplets \( (n_0, k_0, \ell_0) \) and the corresponding resonance conditions.

<table>
<thead>
<tr>
<th>( n_0 )</th>
<th>( k_0 )</th>
<th>( \ell_0 )</th>
<th>Resonance condition</th>
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<tbody>
<tr>
<td>±n₀</td>
<td>±1</td>
<td>½</td>
<td>( n=n₀ ) Hartmann-Hahn condition (zero-quantum cross polarization)</td>
</tr>
<tr>
<td>±1</td>
<td>±1</td>
<td>0</td>
<td>( n=n₀ ) Hartmann-Hahn condition (double-quantum cross polarization)</td>
</tr>
<tr>
<td>±1</td>
<td>½</td>
<td>0</td>
<td>HORROR condition of spin ( I )</td>
</tr>
<tr>
<td>±2</td>
<td>±2</td>
<td>0</td>
<td>( n=1 ) Rotary-resonance condition of spin ( I )</td>
</tr>
<tr>
<td>±3</td>
<td>±2</td>
<td>0</td>
<td>( n=2 ) HAMORR conditioner of spin ( I )</td>
</tr>
<tr>
<td>±4</td>
<td>0</td>
<td>½</td>
<td>( n=n₀ ) Rotary-resonance condition of spin ( S )</td>
</tr>
<tr>
<td>±1</td>
<td>0</td>
<td>½</td>
<td>HORROR condition of spin ( S )</td>
</tr>
<tr>
<td>±2</td>
<td>0</td>
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<td>( n=1 ) Rotary-resonance condition of spin ( S )</td>
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<tr>
<td>±3</td>
<td>0</td>
<td>±2</td>
<td>( n=2 ) HAMORR conditioner of spin ( S )</td>
</tr>
</tbody>
</table>

\[
\overline{\hat{H}} = \hat{H}^{(0,0,0)} + \hat{H}^{(0,-1,1)} + \hat{H}^{(n,1,-1)} = \sum_{\ell < m} \omega_r^{(0)} \hat{I}_\ell \cdot \hat{B}_m + \sum_{p<q} \omega_r^{(0)} \hat{S}_p \cdot \hat{S}_q + \sum_{p=1}^{N_S} \left( \frac{1}{2} \sum_{p=1}^{N_S} \left( \omega_r^{(+)} \hat{t}_S^{(r)} + \omega_r^{(-)} \hat{t}_S^{(s)} \right) \right). \tag{26}
\]

It contains again the homonuclear \( J \) couplings and the flip-flop terms of the heteronuclear dipolar couplings that promote the heteronuclear polarization transfer. In the case of double-quantum polarization transfer, the zero-quantum operators have to be replaced by double-quantum operators. The \( n = \pm 1, \pm 2 \) conditions can clearly be seen in Figs. 2(d) and 2(e) at \( (\omega_{1f} - \omega_{1S})/\omega_r = \pm 1 \) and \( \pm 2 \) as polarization transfer from \( S_I \) to the \( I \) spin.

The Hartmann-Hahn conditions can also be described using average Hamiltonian theory due to the fact that a single frequency, namely \( \omega_r \), can be used to describe the time dependence of the spin-system Hamiltonian. The Floquet results shown in Eqs. (25) and (26) agree with the results obtained by AHT. The Floquet-theory-based effective Hamiltonian formalism presented here has the advantage that all resonance conditions can be obtained in a single ansatz. The different resonance conditions are distinguished only in the selection of the Fourier coefficients that are important for the given experiment.

### 2. Rotary-resonance-type conditions

Besides the Hartmann-Hahn matching conditions which depend on the rf-field amplitudes \( \omega_{1f} \) and \( \omega_{1S} \), there are additional resonance conditions that involve the rf-field amplitude of a single spin species and lead only to homonuclear polarization transfer or a recoupling of the CSA tensor. They are called rotary-resonance conditions and involve the matching of a rf-field amplitude \( \omega_{1f} \) to a multiple or submultiple of the spinning frequency. The \( n=1 \) rotary-resonance condition for the \( I \) spins is found for \( (n_0, k_0, \ell_0) = (\pm 1, \mp 1, 0) \) and \( (n_0, k_0, \ell_0) = (\pm 2, \mp 2, 0) \) with an effective Hamiltonian of

\[
\overline{\hat{H}} = \hat{H}^{(0,0,0)} + \hat{H}^{(1,0,-1)} + \hat{H}^{(-1,0,1)} + \hat{H}^{(2,0,2)} = \sum_{\ell < m} \omega_r^{(0)} \hat{I}_\ell \cdot \hat{I}_m + \sum_{p<q} \omega_r^{(0)} \hat{S}_p \cdot \hat{S}_q + \sum_{p=1}^{N_S} \left( \omega_r^{(1)} \hat{S}_p - \frac{1}{2} \sum_{p=1}^{N_S} \omega_r^{(2)} \hat{S}_p \cdot \hat{S}_q \right) + \omega_r^{(-1)} \hat{S}_p + \frac{3}{4} \sum_{\ell < m} \omega_r^{(2)} \hat{S}_p \cdot \hat{S}_q + \omega_r^{(-2)} \hat{S}_p \cdot \hat{S}_q. \tag{27}
\]

The \( n=1 \) rotary-resonance condition for the \( S \) spin at \( (n_0, k_0, \ell_0) = (\pm 1, \mp 1, 0) \) and \( (n_0, k_0, \ell_0) = (\pm 2, \mp 2, 0) \) has an equivalent Hamiltonian with \( I \) and \( S \) spins interchanged. The Hamiltonian contains, besides the homonuclear \( J \) couplings, the recoupled chemical-shift tensor components and the homonuclear dipolar couplings. In contrast to the rotary-resonance experiment with irradiation on the \( I \) spin only, the heteronuclear dipolar coupling is not contained in the effective Hamiltonian of the double-irradiation experiment.

The \( n=2 \) rotary-resonance condition for the \( I \) spins is found for \( (n_0, k_0, \ell_0) = (\pm 2, \mp 2, 0) \) with an effective Hamiltonian of

\[
\overline{\hat{H}} = \hat{H}^{(0,0,0)} + \hat{H}^{(2,0,2)} = \sum_{\ell < m} \omega_r^{(0)} \hat{I}_\ell \cdot \hat{I}_m + \sum_{p<q} \omega_r^{(0)} \hat{S}_p \cdot \hat{S}_q + \sum_{p=1}^{N_S} \left( \omega_r^{(2)} \hat{S}_p \cdot \hat{S}_q + \omega_r^{(-2)} \hat{S}_p \cdot \hat{S}_q \right). \tag{28}
\]

The \( n=2 \) rotary-resonance condition for the \( S \) spins has an equivalent Hamiltonian with \( I \) and \( S \) spins interchanged. Comparing the effective Hamiltonian of Eq. (28) with the effective Hamiltonian of the \( n=2 \) rotary-resonance experiment with irradiation of the \( I \) spin only, shows that the heteronuclear dipolar coupling is recoupled only in the latter experiment. Only chemical-shift terms are retained in the effective Hamiltonian which has been exploited to measure CSA tensors under MAS.

The HORROR condition for the \( I \) spins is characterized by \( (n_0, k_0, \ell_0) = (\pm 1, \mp 2, 0) \) leading to an effective Hamiltonian of...
Here we obtain (besides the homonuclear J couplings) a purely homonuclear dipolar-coupling Hamiltonian that is the same as the one for the irradiation of a single spin species. The n = 1, 2 rotary-resonance conditions lead to a broadening of the lines due to a reintroduction of the CSA tensor as can be seen in Fig. 2(g) at $\omega_{15}/(2\pi) = 20$ and 40 kHz. The HORROR condition leads to a homonuclear double-quantum polarization transfer as indicated by the negative intensity of spin $S_2$ at $\omega_{15}/(2\pi) = 10$ kHz in Fig. 2(i). Such an experiment can only be described by AHT if one assumes that the rf-field amplitude on the $I$ spins is a multiple of the MAS frequency. The results obtained using here are correct for all values of $\omega_I$. 

**B. Second-order resonance conditions**

Higher-order resonance conditions appear first in the second-order contributions $\mathcal{H}^{(2)}(n_0,k_0,\ell_0)$ to the off-diagonal Floquet blocks. In this section we will only discuss contributions to resonance conditions that do not appear as first-order resonance conditions. There are of course also second-order contributions to all the first-order resonance conditions discussed in the previous section but they lead only to small corrections under conditions where the Floquet treatment is valid. The only exception to this is the $n=0$ Hartmann-Hahn condition where the second-order contributions from the dipolar couplings can be significantly larger than the zeroth-order contributions from the J couplings of Eq. (25).

In second order the allowed ranges for the indices in the $\mathcal{H}^{(2)}(n_0,k_0,\ell_0)$ terms are given by $n_0 = -4, \ldots , 4$, $k_0 = -4, \ldots , 4$, and $\ell_0 = -4, \ldots , 4$. This extended range leads to the appearance of new Hartmann-Hahn cross-polarization conditions that involve the rf field of both spins and of new rotary-resonance conditions that involve only the rf field of a single spin. Rotary-resonance condition can only lead to homonuclear polarization transfer or a recoupling of the CSA tensor while Hartmann-Hahn conditions can induce homonuclear or heteronuclear polarization transfer. All possible resonance conditions that have nonzero Floquet blocks up to second order in the perturbation treatment can be found in Table I.

### 1. Hartmann-Hahn matching conditions

Higher-order Hartmann-Hahn conditions appear in the second-order contributions only with the combinations $(n_0,k_0,\ell_0)=(n_0, \pm 1, \pm 1)$, where $n_0$ can assume all values from −4 to 4. In second order, there are no contributions to the Hartmann-Hahn conditions from terms with $|\ell_0| > 1$. The second-order contributions to the $n = n_0$ Hartmann-Hahn condition can be expressed in a general form as

$$\mathcal{H}^{(n_0,1,1)} = \mathcal{H}^{(0,0,0)} + \mathcal{H}^{(2)}(n_0,1,1) + \mathcal{H}^{(2)}(2n_0,1,1),$$

with
Here, a given $n_0$ can assume values from −4 to 4 and the summation restriction $n_0 = \nu + \nu'$ needs to be fulfilled.

In second order, the $n=3$ and the $n=4$ Hartmann-Hahn conditions appear as new resonance conditions. The effective Hamiltonian contains cross terms between the homonuclear and the heteronuclear dipolar couplings and promotes heteronuclear polarization transfer through the three-spin zero-quantum terms of Eq. (31). It is important to remember that for the second-order resonance conditions one has to take into account the zeroth-order and second-order contributions to the central block of the Floquet Hamiltonian.

The polarization transfer from the $S_1$ to the $I$ spin can be seen in Figs. 2(d) and 2(e) at $(\omega_{11} - \omega_{13})/\omega_r = 0, \pm 3$, and $\pm 4$. It is apparent that the width of the higher-order Hartmann-Hahn matching conditions is much narrower due to the smaller magnitude of these terms. These conditions can also be described using higher-order terms in the average Hamiltonian expansion.

2. Rotary-resonance conditions

The higher-order rotary-resonance conditions appear in the second order only for the combinations $(n_0, 0, \ell_0)$ and $(n_0, k_0, 0)$ where $n_0$ can assume values from −4 to 4 and $k_0$ or $\ell_0$ values from −2 to 2. The effective Hamiltonians for the second-order contributions are given by

$$\hat{H}^{(n_0,0,1)} = \hat{H}^{(0,0,0)} + \hat{H}^{(0,0,1)} + \hat{H}^{(n_0,0,−1)} + \hat{H}^{(−n_0,0,0)},$$

with

$$\hat{H}^{(0,0,0)} = \sum_{\nu,\nu',\ell} \frac{\omega_{11}(2\omega_{11}^2 - \omega_{11}^2 + 2\nu \omega_r(\omega_{13} - \nu \omega_r))}{2(\omega_{11} - \nu \omega_r)(\omega_{13} - \nu \omega_r)^2} S_{\nu}^z I_{\ell} S_{\nu'}^z,$$

$$- \sum_{\nu,\nu',\ell < m} \frac{\omega_{15} \omega_{15}^{(z)} S_{\nu}^z S_{\nu'}^z}{8} \left( \frac{18 \omega_{15}^{(z)}}{(2\omega_{13} - \nu \omega_r)(\omega_{13} + \nu \omega_r)} + \frac{\omega_{15}^{(z)} + 2\omega_{15}^{(z)}}{\nu \omega_r(\omega_{13} - \nu \omega_r)} \right) S_{\nu}^z S_{\nu'}^z$$

$$- \sum_{\nu,\nu',\ell < m} \frac{\omega_{15} \omega_{15}^{(z)} S_{\nu}^z S_{\nu'}^z}{8} \left( \frac{18 \omega_{15}^{(z)}}{(2\omega_{13} - \nu \omega_r)(\omega_{13} + \nu \omega_r)} + \frac{2\omega_{15}^{(z)} + \omega_{15}^{(z)}}{\nu \omega_r(\omega_{13} - \nu \omega_r)} \right) S_{\nu}^z S_{\nu'}^z,$$

for $(n_0, 0, 1)$ and by

$$\hat{H}^{(n_0,0,2)} = \hat{H}^{(0,0,0)} + \hat{H}^{(0,0,1)} + \hat{H}^{(n_0,0,−2)} + \hat{H}^{(−n_0,0,0)},$$

with

$$\hat{H}^{(0,0,2)} = - \sum_{\nu,\nu',\ell < m} \frac{3\omega_{13}(\omega_{13}^{(z)} S_{\nu}^z S_{\nu'}^z + \omega_{13}^{(z)} S_{\nu}^z S_{\nu'}^z + 2(\omega_{13}^{(z)} S_{\nu}^z S_{\nu'}^z + \omega_{13}^{(z)} S_{\nu}^z S_{\nu'}^z))}{8 \nu \omega_r(\omega_{13} - \nu \omega_r)}$$

$$\times (S_{\nu}^z S_{\nu'}^z S_{m}^z S_{n}^z + S_{\nu}^z S_{m}^z S_{n}^z S_{\nu'}^z + S_{\nu}^z S_{m}^z S_{n}^z S_{m}^z S_{n}^z + S_{\nu}^z S_{m}^z S_{n}^z) + \sum_{\nu,\nu',\ell < m} \frac{\omega_{11}(\omega_{11}^{(z)} S_{\nu}^z S_{\nu'}^z + \omega_{11}^{(z)} S_{\nu}^z S_{\nu'}^z)}{2(\omega_{11} - \nu \omega_r)^2(\omega_{13} - \nu \omega_r)^2} S_{\nu}^z S_{\nu'}^z I_{\ell} S_{\nu}^z S_{\nu'}^z,$$

for $(n_0, 0, 2)$. Again, the summation restriction $n_0 = \nu + \nu'$ has to be fulfilled. The effective second-order Hamiltonians for the resonance conditions $(n_0, 1, 0)$ and $(n_0, 2, 0)$ can easily be obtained by exchanging the $I$ and $S$ spin indices in Eqs. (33) and (35).

We find in second order three new resonance conditions: the $n=3$ and the $n=4$ rotary-resonance condition and a generalized HORROR condition at $\omega_{1} = \frac{3}{2} \omega_0$. At the higher-order rotary-resonance conditions we obtain homonuclear and heteronuclear coupling terms that originate from cross terms between the CSA tensor and homonuclear or heteronuclear dipolar couplings. They lead to a broadening of the resonance line. The $3/2$ HORROR condition we find homonuclear double-quantum polarization transfer mediated...
through three-spin terms. We have verified the 3/2 HORIZOR condition by simulations and experiment (data not shown). The magnitude of the recoupling Hamiltonian, however, is small and it is not clear whether there are any practical application of this new HORIZOR condition.

Figure 2(g) shows that the \( n=3 \) and 4 rotary-resonance conditions at \( \omega_{15}/(2\pi)=60 \) and 80 kHz are quite weak. The \( \frac{3}{2} \) HORIZOR condition is visible as polarization transfer to the \( S_2 \) spin at \( \omega_{15}/(2\pi)=30 \) kHz but is also quite weak. These resonance conditions can only be described by AHT if we assume that the \( I \)-spin rf-field amplitude is a multiple of the MAS frequency.

C. Third-order resonance conditions

In the third-order contribution to the effective Hamiltonian, the allowed ranges of values are \( n_0=-6, \ldots, 6 \), \( k_0=-6, \ldots, 6 \), and \( \ell_0=-6, \ldots, 6 \). The third-order effective Hamiltonian will of course contribute to first-order and second-order resonance conditions. In addition, we find some new resonance conditions that are not allowed in lower orders of the Hamiltonian. The third-order terms are, typically, small compared to contributions of lower order and may only be relevant for experiments utilizing pure second-order effects. As one example, the set of recoupling conditions connected to the combinations \((n_0,k_0,\ell_0)=(0,1,\pm 2)\) \((n_0,k_0,\ell_0)=(0,1,\pm 3)\) shall be mentioned here. The effective Hamiltonian for these resonance conditions consists of three-spin and four-spin terms \( S_2^z\overline{S}_0^z, S_2^z\overline{S}_m^zS_n^z \) originating from cross terms between two heteronuclear dipolar couplings and one CSA, cross terms between three heteronuclear dipolar couplings, or cross terms between two homonuclear dipolar couplings and one heteronuclear dipolar coupling. That leads to partial recoupling of heteronuclear dipolar couplings and thus to a line broadening of the observed signal at this resonance condition.

D. Outside any resonance condition

Here, we consider the case where no resonance condition is matched in our system, e.g., \( n_0, k_0, \ell \omega_{15} \neq 0 \) for all possible combinations of the allowed values \( n=-2, -1, 0, 1, 2, k=-2, -1, 0, 1, 2, \) and \( \ell =-2, -1, 0, 1, 2 \). The contributions to the effective Hamiltonian calculated here are also important in the case of any resonance conditions as discussed in the previous three sections since they always contribute to the effective Hamiltonian.

Far away from any resonance conditions there are no degenerate states in the Fourier space of the Floquet Hamiltonian and we only need to take into account the diagonal contribution \( \hat{\mathcal{H}}^{(0,0,0)} \) for the effective Hamiltonian. Therefore, the effective Hamiltonian is given by

\[
\hat{\mathcal{H}} = \hat{H}^{(0,0,0)} + \hat{H}^{(2,0,0)} + \cdots = \hat{H}^{(0,0,0)}
\]

with

\[
\hat{H}^{(0,0,0)} = \sum_{\ell < m} \omega_{15}^{(0)} \mathbf{I}_{\ell m} \cdot \mathbf{I}_{m \ell} + \sum_{p < q} \omega_{15}^{(0)} \mathbf{S}_p \cdot \mathbf{S}_q.
\]

Only the homonuclear \( J \) couplings that are isotropic in spin and real space contribute in zeroth order. The second order of the effective Hamiltonian can be calculated by inserting the Fourier coefficients of Eq. (24) into Eq. (36) and one obtains...
There are three different types of terms in this second-order contribution to the effective Hamiltonian: (i) Terms containing $I_{mc}$ or $S_{pc}$ operators that represent fictitious fields along the direction of the applied rf fields. They originate from cross terms between the heteronuclear dipolar or $J$ coupling, the homonuclear dipolar coupling, or the chemical-shift tensor with itself. Such fictitious-field terms lead to a mismatch of resonance conditions from the theoretical values of the rf-field amplitude as has been observed experimentally in the case of single-spin cw irradiation.\(^{18}\) (ii) Homonuclear three-spin terms of the form $2I_{1c}F_{mc}S_{c}^{-}$ and $2S_{c}F_{mc}S_{c}^{-}$ that promote spin diffusion in the rotating frame on the $I$ and $S$ spins, respectively. They originate from cross terms between two homonuclear dipolar couplings which have one spin in common. (iii) Heteronuclear three-spin terms of the form $2S_{c}I_{mc}F_{mc}^{-}$ and $2I_{mc}S_{c}S_{mc}^{-}$ that promote spin diffusion in the rotating frame on the $I$ and $S$ spins, respectively. They originate from cross terms between two heteronuclear dipolar couplings that have the $S$ or $I$ spin in common. The transitions that are allowed under such a three-spin $2I_{1c}F_{mc}S_{c}^{-}$ operator is illustrated by arrows in the energy-level diagram of a three-spin-1/2 system shown in Fig. 3. They correspond to the two zero-quantum transitions of the $I_{2}I_{3}$ subsystem.

In the simulations, the nonresonant second-order contribution is manifest as a homonuclear polarization transfer from spin $S_{1}$ to spin $S_{2}$ close to the diagonal in Fig. 2(c) which corresponds to the broad intensity of spin $S_{2}$ in Fig. 2(f) in the center of the spectrum. This homonuclear polarization transfer is mediated by the heteronuclear three-spin terms of Eq. \(38\) and forms the basis of the TSAR experiment.\(^{32}\) The TSAR zero-quantum polarization transfer is very similar to the polarization transfer in proton-driven spin diffusion under MAS.\(^{33}\) Figure 4(a) shows the expectation value $\langle S_{2z} \rangle$ for a mixing time of 10 ms in a full time-dependent numerical simulation of the $I_{2}I_{3}$ three-spin system including only heteronuclear dipolar couplings. This clearly confirms that the homonuclear dipolar coupling does not play a role in this experiment, as already described in Ref. 32 on the basis of numerical simulations.

In principle, the polarization transfer under the Hamiltonian of Eq. \(38\) does not depend on any resonance conditions and should be broadband with respect to the magnitude of the applied rf-field amplitudes. Figure 4(a), however, shows that there is a strong dependence of the amount of polarization transfer after 10 ms mixing time on the rf-field amplitudes. This dependence cannot be explained by the change in the magnitude of the three-spin term as can be seen from an effective Hamiltonian calculation [Fig. 4(b)] that only takes into account the heteronuclear three-spin terms of Eq. \(38\). Only if we also include the fictitious-field terms (see above) in the effective Hamiltonian simulations [Fig. 4(c)] can we find a satisfactory agreement between the effective Hamiltonian and the full numerical simulations. In fact, the maximum of the polarization transfer is reached at the point where the fictitious-field terms are zero. This shows that the polarization transfer is partially quenched by the fictitious fields. Since the polarization transfer in the TSAR experiment is mediated by second-order three-spin terms as is the case in proton-driven spin diffusion, it is expected that...
such an experiment shows a reduced sensitivity to dipolar truncation compared to recoupling experiments that generate a double-quantum or a zero-quantum Hamiltonian in zeroth-order approximation.33

IV. CONCLUSIONS

In this work, we present a trimodal operator-based Floquet formalism to describe solid-state NMR experiments with three incommensurate frequencies. To validate such a description, we used the example of MAS with simultaneous irradiation of two different spin species. All the well known resonance conditions can be identified and characterized by effective Hamiltonians within a single theoretical formalism.

We could also characterize the effective Hamiltonian that describes the homonuclear TSAR polarization transfer.32

Multimode operator-based Floquet theory allows the description of NMR experiments with multiple time-dependent interactions in a concise and unified way that does not depend on the detailed structure of the Hilbert-space Hamiltonian if the relevant frequencies are larger than the spectral range of the effective Hamiltonian. Thus, the intermediate step into the Floquet space can be seen as a black box, which has to be solved only once for a given dimensionality of the time-dependent problem. This allows the application of effective Hamiltonians derived from Floquet theory [see Eqs. (18)–(20)] in a way very similar to average Hamiltonian theory.

There are other important problems in solid-state NMR that have three incommensurate frequencies and can be treated by the formalism presented in this paper. One important example of such an experiment that can only be described without approximations concerning the flip angle using trimodal Floquet theory is the TPPM (Ref. 29) decoupling sequence which will be treated in a forthcoming publication. Other problems that are amenable to the treatment presented here are cw decoupling while a rotor-synchronized recoupling sequence is applied to another nuclei.

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APPENDIX: FOURIER COEFFICIENTS UNDER MAS

The Fourier coefficients of the Hamiltonian of Eq. (22) are defined in agreement with Ref. 34. The Fourier coefficients of the chemical-shift Hamiltonian are given by

\[ \omega^{(n)}_{sp} = \frac{2}{\sqrt{6}} d^2_{n,0}(\theta_r) e^{-i\gamma} \sum_{m=-2}^{2} d^2_{m,n}(\beta) e^{-i\alpha \rho^{(S)}_{2,m}} \] (A1)

for \( n \neq 0 \) and

\[ \omega^{(0)}_{sp} = \omega^{(0)}_{sp} \] (A2)

for \( n=0 \). Here, \( d^2_{m,n}(\beta) \) is the reduced Wigner matrix element; \( \theta_r \) is the rotation angle; \( \alpha, \beta, \) and \( \gamma \) are the three Euler angles which describe the orientation of the chemical-shift tensor in the rotor-fixed frame; and \( \rho^{(S)}_{2,m} \) are the elements of the chemical-shielding tensor in spherical-tensor notation. They are defined as

FIG. 4. Numerical simulations of polarization transfer in the TSAR experiment using the same heteronuclear IS three-spin system as in Fig. 2 taking into account only the heteronuclear dipolar couplings. The spinning frequency was set to 20 kHz. The rf amplitude was set to \( \nu_1=90 \) kHz, and the rf-field amplitude of the I spin was varied between 0 and 150 kHz. (a) A simulation using the full time-dependent Hamiltonian is shown in comparison to effective Hamiltonian simulations using (b) only the homonuclear transfer terms and (c) the homonuclear transfer term plus the fictitious-field terms as shown in Eq. (38).
\[ \rho^{(S)}_{2,0} = \sqrt{\frac{3}{2}} \delta^{(S)}_{\alpha \beta}, \]
\[ \rho^{(S)}_{2,\pm 1} = 0, \]
\[ \rho^{(S)}_{2,\pm 2} = -\frac{1}{2} \delta^{(S)}_{\alpha \beta} \eta^{(S)}_{\alpha \beta}. \]  
(A3)

Here, the anisotropy of the chemical-shift tensor, \( \delta^{(S)}_{\alpha \beta} \), is defined in angular frequency units and \( \eta^{(S)}_{\alpha \beta} \) is the asymmetry of the chemical-shift tensor.

The Fourier coefficients for the dipolar-coupling tensors are defined as
\[ \omega^{(n)}_{m} = \frac{1}{\sqrt{6}} |d_{m}(\theta) e^{-i n \phi} d_{0,n}(\beta) \rho^{(I)}_{2,0} | d_{m}(\theta) e^{-i n \phi} d_{0,n}(\beta) \rho^{(I)}_{2,0} \]
\[ = \frac{1}{\sqrt{3}} \delta^{(I)}_{m} d_{0,n}(\beta) e^{-i n \phi} \delta_{D}^{(I)}(m) \]
\[ (\text{for } \theta_{n} = \theta_{m} = 54.74^\circ) \]  
(A4)

with \( n \neq 0 \) where \( d_{m}(\beta) \) is the reduced Wigner matrix element; and the angles \( \beta \) and \( \gamma \) are the two Euler angles describing the orientation of the dipolar-coupling tensor in the rotor-fixed frame. The spherical-tensor elements are given by
\[ \rho^{(I)}_{2,0} = \frac{1}{\sqrt{2}} \delta^{(I)}_{D} \]  
(A5)

and for \( m \neq 0 \)
\[ \rho^{(I)}_{2,m} = 0. \]  
(A6)

Here,
\[ \delta^{(I)}_{D} = -\frac{2 \mu_{0} \gamma \gamma \hbar}{4 \pi r_{0}^{3}} \]  
(A7)

is the anisotropy of the dipolar-coupling tensor in units of angular frequency. The second line of Eq. (A4) is only valid for \( \theta_{n} = \theta_{m} = 54.74^\circ \) (magic angle). For the heteronuclear dipolar-coupling tensor, analogous expressions hold true.

The Fourier coefficient of the homonuclear \( J \) couplings is defined as
\[ \omega^{(0)}_{m} = 2 \pi J_{m} \]  
(A8)

while the Fourier coefficient of the heteronuclear \( J \) coupling is defined as
\[ \omega^{(n)}_{m \neq p} = \pi J_{m \neq p} \]  
(A9)