

Theory of heteronuclear decoupling in solid-state nuclear magnetic resonance using multipole-multimode Floquet theory

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A formal theory for heteronuclear decoupling in solid-state magic angle spinning (MAS) nuclear magnetic resonance experiments is presented as a first application of multipole-multimode Floquet theory. The method permits a straightforward construction of the multispin basis and describes the spin dynamics via effective Floquet Hamiltonians obtained using the van Vleck transformation method in the Floquet–Liouville space. As a test case, we consider a model three-spin system (I_2S) under asynchronous time modulations (both MAS and rf irradiation) and derive effective Hamiltonians for describing the spin dynamics in the Floquet–Liouville space during heteronuclear decoupling. Furthermore, we describe and evaluate the origin of cross terms between the various anisotropic interactions and illustrate their exact contributions to the spin dynamics. The theory presented herein should be applicable to the design and understanding of pulse sequences for heteronuclear and homonuclear recoupling and decoupling. © 2005 American Institute of Physics. [DOI: 10.1063/1.1875112]

I. INTRODUCTION

High resolution solid-state nuclear magnetic resonance (NMR) has emerged as a powerful tool for the elucidation of molecular structure and dynamics in systems not amenable to characterization by other techniques. These include both microscopically ordered preparations such as membrane proteins,^{1,2} nanocrystalline proteins,^{3,4} and amyloid fibrils,^{5,6} and also disordered or amorphous systems such as glasses.⁷ In solid-state NMR spectra of spin-1/2 nuclei, site-specific resolution can be obtained either by uniaxial orientation of the sample with respect to the static magnetic field^{2,8} or, more generally, through magic angle spinning (MAS).⁹ In the latter case, manipulation of the spatial part of the Hamiltonian by sample spinning results in isotropiclike spectra that resemble those obtained in the solution state, at least for dilute nuclei such as ¹³C and ¹⁵N in biopolymers or other organic solids. Methods based on MAS NMR have now matured to the point where complete structure determination is possible.^{4,5,10}

However, the line-narrowing effects of MAS alone are inadequate for spectral resolution at current accessible spinning frequencies, particularly for abundant nuclei which are strongly coupled (e.g., ¹H in organic solids).¹¹ One consequence is that the ¹H spectroscopy in most solids is not routinely possible; a second consequence is that, even under MAS, the spectra of dilute nuclei such as ¹³C and ¹⁵N continue to be broadened through residual interactions with neighboring protons. This situation can be ameliorated but not completely resolved through the application of spin de-

coupling, which amounts to an averaging in spin space^{12,13} of the couplings responsible for the residual broadening by the action of rf pulses.

The simplest heteronuclear decoupling scheme involves high power, continuous wave (CW) on-resonance irradiation of the protons during detection of the heteronuclei. In general, linewidths improve as the decoupling field strength approaches and exceeds the strength of the heteronuclear dipolar couplings. However, several features of the spin dynamics during CW decoupling (and also other decoupling techniques) suggest that more complicated processes are at work.¹⁴ For example, when the modulation due to MAS and decoupling occur on similar time scales, interference effects or recoupling of the heteronuclear dipolar interactions occur in the vicinity of several matching conditions.¹⁵ In addition, interesting experimental observations by Tekely *et al.*,¹⁶ and Ernst *et al.*¹⁷ suggest that the homonuclear dipolar interaction among the protons plays a beneficial role in spin decoupling, thereby resulting in narrower lines than would otherwise be observed. This phenomenon of “self-decoupling” has been rationalized according to semiclassical models of ¹H–¹H spin diffusion. Such observations have further been validated in the observed decrease in the decoupling efficiency during Lee–Goldberg irradiation¹⁸ of the abundant spins (where the decoupling field is applied off-resonance so as to align the effective field along the magic angle), a fact which is consistent with the principle of self-decoupling.

Over the last decade, a few multiple-pulse decoupling sequences were developed in an effort to improve upon the performance of CW decoupling. The earliest and one of the most successful examples of these sequences is the two-pulse phase modulated (TPPM) decoupling sequence of Bennett *et al.*,¹⁹ which consists of two $\sim 180^\circ$ pulses with a small phase difference ($\pm\phi$) between them. Under essentially all circum-

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stances, TPPM yields a factor of 2–5 improvement in linewidths over those observed with CW decoupling of the same field strength. Recently, a particularly simple variant of this sequence was introduced in which the pulse phases were chosen to have a phase difference of 180° , thereby requiring only the pulse width to be optimized. The resulting “XiX” sequence²⁰ offers significant advantages over TPPM decoupling at high spinning frequencies, but at low or moderate spinning frequencies, few differences are observed. In both cases, contributions to the residual linewidth during high power decoupling have been partially enumerated but not completely understood.

In this regard, Sachleben *et al.*¹⁴ presented an analytical treatment of CW decoupling in static solids using the concept of effective Hamiltonians obtained via the Van Vleck (or contact) transformation method. To second order, the spectrum of an $I_N S$ system consists of a centerband and several decoupling sidebands; as the decoupling field strength is increased, the sidebands decrease in intensity and increase in frequency offset from the centerband, while the centerband line shape remains fixed (at least for on-resonance decoupling). Explicit simulations of an $I_7 S$ spin system show that the on-resonance sideband effects are the dominant contribution to the observed linewidths. This contradicts the predictions of an earlier theory of decoupling, due to Mehring and co-workers,²¹ in which the ^1H 's are treated in a semiclassical continuum model using a Gaussian memory function representation. The latter approach predicts that on-resonance decoupling will result in a narrowing of the resonance line with increasing decoupling field strength.

In a variety of cases, MAS experiments have been successfully analyzed using average Hamiltonian theory (AHT),^{12,22} which yields an effective Hamiltonian averaged over some cycle time of a periodic pulse sequence. A prerequisite of this approach, therefore, is that all the time modulations be synchronized with the sample rotation and that the sampling be stroboscopic in that period or its multiples. Using this approach, Gan and Ernst²³ designed a frequency-modulated analog of TPPM and explored other possibilities involving simultaneous phase and frequency modulation. Their theoretical study based on zero-order average Hamiltonians suggest, in agreement with the earlier results of Bennett *et al.*,¹⁹ that the improved performance of TPPM over CW decoupling results partially from a so-called “second averaging,” in which higher-order terms in the effective Hamiltonian are canceled by the nutation imposed by phase or frequency modulation. Nevertheless, they neither enumerate the higher-order contributions nor discuss their relative magnitudes. Elaborating upon this approach, Ernst *et al.*,²⁴ attributed the dominant contribution to the residual linewidth under MAS and decoupling to a cross term in the second-order average Hamiltonian between the chemical shift anisotropy (CSA) of the I spin and the heteronuclear dipolar coupling that in principle cannot be completely averaged by MAS alone.

In a similar vein, Eden and Levitt utilized symmetry arguments²⁵ based on AHT and attempted to explicitly construct optimized heteronuclear decoupling sequences²⁶ involving rotor-synchronized pulse sequences whose funda-

mental element (“C” element) is an effective 2π pulse. Following the experimental observations and arguments previously cited, their sequences were designed to (i) decouple the heteronuclear dipolar interaction, (ii) actively *recouple* the homonuclear dipolar interaction among the protons, and (iii) scale the cross terms in the second-order average Hamiltonian between the ^1H CSA and the heteronuclear dipolar coupling or between the homonuclear and heteronuclear dipolar couplings. Unfortunately, the resulting Cl_2^{-1} family of sequences offer no experimental improvement over TPPM decoupling, and are often impractical to implement at higher MAS frequencies. In particular, they are $N=6$ sequences that require high decoupling rf field strengths $\omega_{rf}=6\omega_r$. This is in contrast to the TPPM decoupling scheme, which can be implemented for arbitrary decoupling field strengths. In view of the limitations of the theory used to construct these sequences—specifically, its validity only for on-resonance decoupling and for rotor-synchronized pulse sequences—it is intriguing that the best experimental results were obtained for *off-resonance* decoupling and in the case where the pulse sequence symmetry was *explicitly broken* or rendered asynchronous. The latter fact suggests that an AHT approach does not completely explain the observed spin dynamics.

Recently, Ernst and co-workers²⁷ also introduced an elegant phenomenological model of heteronuclear decoupling which accounts for multiple coupled ^1H spins in Liouville space and explains the salient features of CW and multiple pulse decoupling. In their approach, an IS system is modeled quantum mechanically through average Hamiltonian theory, while the coupling among the I spins in the proton spin bath is described through a classical spin diffusion-type superoperator in Liouville space. Further, the spin diffusion process is assumed to be isotropic and is characterized only by a single rate constant. In the CW case, the theory predicts a pronounced self-decoupling effect as the spin diffusion rate constant increases. The superior performance of multiple-pulse decoupling schemes is rationalized as an attenuation of the second-order cross terms which contribute to the residual linewidth. Though the approach appears to explain some aspects of heteronuclear decoupling which previous approaches do not, further study is still warranted.

The difficulty of formulating the decoupling problem with acceptable fidelity to experimental results suggests that direct numerical optimization may be a simpler route to improved heteronuclear decoupling sequences. Such approaches have been followed by several authors in the case of static solids, but with out any improvement under MAS conditions. Recognizing the limitations in the model employed for the description of spin dynamics under MAS, De Paeppe *et al.*²⁸ recently abandoned the *in silico* approach altogether in favor of direct optimization on the NMR spectrometer. In their approach, the phase of the rf during decoupling is expressed in a Fourier series, and the Fourier coefficients are varied using a simplex optimization scheme in order to minimize the linewidth. The optimal result consistently involves only a single cosinusoidal modulation of the phase. The simplicity of this result suggests that a sophisticated description of the spin dynamics might yield the same outcome on analytical grounds alone and, indeed, the phase

modulation is extremely similar to that of TPPM. The performance of numerically optimized sequences is comparable to that of TPPM or XiX decoupling. Recently, Emsley and co-workers²⁸ made an interesting experimental observation by measuring the residual linewidths obtained from a simple spin echo experiment.²⁸ Their results suggest large differences in the refocused linewidths of the ¹³C resonances for different decoupling sequences. Although the one-dimensional spectra look more or less identical, the refocused linewidth measurements necessitate a deeper understanding of the spin dynamics under heteronuclear decoupling. The differences in the refocusable T_2 measurements for various heteronuclear decoupling sequences may arise from a coherent contribution to the relaxation dynamics arising from the higher-order corrections in the form of cross terms between the various interactions present in the system. Depending on the decoupling scheme, the magnitude of the cross terms vary and result in different dephasing of the spin polarizations or coherences thereby leading to different refocused linewidth measurements. Similar arguments were proposed by Khitrin and co-workers²⁹ in their description of the SPINAL decoupling scheme based on the correlation function approach. Understanding the role of higher-order corrections, in many solid-state NMR homonuclear and heteronuclear recoupling experiments, in principle, requires explicit consideration of the particular pulse sequence on the heteronuclear channel. The model presented here is generic and results in an effective Hamiltonian for a spin system during heteronuclear decoupling alone. More specific cases are currently being investigated and will be reported in future publications based on the multipole-multimode Floquet theory (MMFT) approach.

In summary, a theory of heteronuclear decoupling in solid-state NMR must explain experimental features such as decoupling sidebands, self-decoupling, interference phenomena, and the superior performance of multiple pulse decoupling sequences such as TPPM and its relatives. In what follows, we develop the bimodal Floquet theory of heteronuclear decoupling, where the Floquet Hamiltonian is expressed using multipole basis operators³⁰⁻³² and the dynamics described in the Floquet–Liouville space. In the Floquet theory, first proposed by Shirley³³ and introduced to NMR by Vega,³⁴ a time-dependent Hamiltonian described in a finite dimensional basis set is transformed into a time-independent Hamiltonian suitably described in an infinite dimensional basis set via Fourier series expansion. The infinite-dimensional basis is constructed using basis states of finite dimension, which have been “dressed” with additional states (also referred as Fourier states) corresponding to each unique time modulation present in the system. The resulting infinite-dimensional Floquet matrices are highly off-diagonal, and their eigenvalues are generally obtained numerically through an iterative truncation procedure based on the convergence of eigenvalues. However, such numerical methods often compromise the analytical insights the formalism might provide into the spin dynamical problem of interest. Here, we propose an alternative to such numerical treatments which preserves this insight in the form of effective Hamiltonians obtained via Van Vleck (or contact) transformation method.³⁵

The contact transformation method first introduced by Van Vleck (1929) is an operator equivalent of the perturbation theory. Unlike the Raleigh–Schrodinger perturbation theory, where perturbation corrections are obtained in terms of matrix elements, the contact transformation method results in corrections in operator form, thereby leading directly to the concept of effective Hamiltonians. The Floquet approach is further simplified by the use of the multipole basis (due to Sanctuary), which exploits the rotational invariance properties of tensor operators, by expressing the basis operators used to describe the spins in terms of irreducible tensor operators thereby aiding a multispin basis to be written almost by inspection for arbitrary spin magnitudes. Further, the evaluation of commutator elements in the spin dynamics calculations can be accomplished in a generic manner using the well-established angular momentum algebra (e.g., Wigner-3J, -6J, -9J symbols).^{36,37} This is in contrast to current existing bases employed in NMR (Ref. 38) (and particularly in Floquet theory³⁹) for spin dynamics calculations, which typically involve multiple commutator relations and are intractable both beyond two spins and for $I > 1/2$. The effective Hamiltonians derived include contributions from the various cross terms and aid in better understanding of the CW, TPPM, and XiX decoupling schemes via a model three-spin system. Differences among these decoupling sequences arise from the magnitudes of terms/cross terms in the Floquet Hamiltonian to second order. In contrast to the AHT approach, which employs the Magnus expansion for the derivation of higher-order terms, the contact transformation procedure enables straightforward evaluation of the higher-order terms. In addition to explaining the spin dynamics for a greater variety of experimental conditions, the theory should be useful in the design of new pulse sequences for homonuclear and heteronuclear decoupling. It is the first application of the MMFT approach introduced in the accompanying paper.⁴⁰

II. THEORY AND DISCUSSION

For the theoretical description of decoupling in solids, we consider a model three-spin system I_2S , where the spins I and S refer to protons (¹H) and carbon (¹³C) (or nitrogen, ¹⁵N) respectively. This approximate model corresponds to a typical arrangement in solids where a dilute spin (such as ¹³C or ¹⁵N) is often coupled to a spin bath of protons. Exploiting the rotational invariance properties of tensor operators, the spin Hamiltonian corresponding to a particular interaction λ is expressed in terms of irreducible tensor operators corresponding to spin ($T^{(k)-q}$) and spatial dimensions ($R^{(k)q}$),⁴¹

$$H = \sum_{\lambda} \sum_{k=0}^2 \sum_{q=-k}^k (-1)^q R_{\lambda}^{(k)q} T^{(k)-q}, \quad (1)$$

with k and q referring to the rank and component of the tensor, respectively. In the rotating frame description, the Hamiltonian is often truncated by retaining only the secular terms (i.e., energy conserving terms involving the $T^{(k)0}$ operators), classified into three categories given below:

$$H = H_S + H_I + H_{IS}. \quad (2)$$

The interactions involving the S -spin system are represented by H_S , and includes the isotropic as well as the anisotropic chemical shift (or chemical shift anisotropy) interactions,

$$H_S = H_S^{CS} + H_S^{CSA} = R_S^{(0)0} T^{(1)0} + R_S^{(2)0} T^{(1)0}. \quad (3)$$

The interactions involving the I spins are represented by H_I and includes the chemical shift (both isotropic as well as anisotropic), scalar coupling and the dipolar interactions,

$$H_I = H_I^{CS} + H_I^{CSA} + H_d^I + H_J^I \\ = R_I^{(0)0} T^{(1)0} + R_I^{(2)0} T^{(1)0} + R_{II}^{(2)0} T^{(2)0} + R_{II}^{(0)0} T^{(0)0}. \quad (4)$$

The heteronuclear interactions are represented by H_{IS} , and includes the dipolar as well as the scalar coupling,

$$H_{IS} = H_d^{IS} + H_J^{IS} = R_{IS}^{(2)0} T^{(2)0} + R_{IS}^{(0)0} T^{(0)0}. \quad (5)$$

During MAS, the anisotropic spatial terms ($R^{(k)0}$, $k \neq 0$) in the Hamiltonian are rendered time dependent and periodic. Since the spatial components $R^{(k)0}$ (corresponding to a particular interaction) are often expressed in their principal axis frames, the following sets of coordinate transformations are necessary for describing the spin dynamics in the lab frame:

$$PAS \xrightarrow{\alpha_{pr}, \beta_{pr}, \gamma_{pr}} RAS \xrightarrow{-\omega_r t, \theta_m, 0} Lab. \quad (6)$$

Such coordinate transformations are effected in the real space (spatial averaging) without affecting the spin operators, by means of Wigner rotation matrices.³⁷ The resulting periodic time-dependent coefficients are expressed conveniently via the Fourier series expansion,⁴¹

$$R_\lambda^{(2)0}(t) = \sum_{m=-2}^2 G_m^\lambda e^{im\omega_r t}, \quad (7)$$

with G_m^λ (where λ corresponds to interactions such as CSA, dipolar, etc.) representing the time-independent Fourier components involving the interaction coefficients.

In a similar vein the effect of radio frequency pulses is described in the rf interaction frame by the unitary transformation function $U_{rf}(t)$

$$\tilde{H}(t) = U_{rf}^{-1}(t) H U_{rf}(t), \quad (8)$$

which in principle can be described as rotations in the spin space, analogous to the rotations in the real space during MAS,

$$D(\Omega_{rf}) T^{(l)m} D^{-1}(\Omega_{rf}) = \sum_{m=-l}^l \alpha_{lm}(t) T^{(l)m}. \quad (9)$$

The notation $\Omega_{rf} = (\alpha + \phi, \beta, \alpha - \phi + \pi)$ represents the set of Euler angles associated with a particular rf field and $T^{(l)m}$ the corresponding irreducible spin tensor operator. The Euler

angles described above have been derived in detail by Sanctuary *et al.*,³² and are governed by the following relations:

$$\cos(\beta) = \frac{1}{\Delta^2} (\delta\omega^2 + \omega_1^2 \cos(\Delta t)), \quad \Delta = \sqrt{\delta\omega^2 + \omega_1^2}, \\ \sin \alpha = \frac{-\cos\left(\frac{\Delta t}{2}\right)}{\sqrt{1 - \frac{\omega_1^2}{\Delta^2} \sin^2\left(\frac{\Delta t}{2}\right)}}, \quad (10)$$

and $\delta\omega$, ω_1 , ϕ_1 , Δ represent the radio frequency offset, amplitude, phase, and effective fields, respectively.

Using the well-known fact that product of two rotations can be represented by a single rotation, i.e.,

$$D_{p,q}^2(\Omega_{AC}) = \sum_{k=-2}^2 D_{p,k}^2(\Omega_{AB}) D_{k,q}^2(\Omega_{BC}), \quad (11)$$

the effect of two pulses is represented by

$$D(\Omega) T^{(l)m} D^{-1}(\Omega) = \sum_{m'} D_{mm'}(\Omega) T^{(l)m'}, \quad (12)$$

where $D(\Omega)$ refers to an effective Wigner rotation matrix [comprises the Euler angle sets $\Omega_1 = (\alpha_1 + \phi_1, \beta_1, \alpha_1 - \phi_1 + \pi)$ and $\Omega_2 = (\alpha_2 + \phi_2, \beta_2, \alpha_2 - \phi_2 + \pi)$ for the two pulses], whose matrix elements are evaluated by the following expression:

$$D_{mm'}(\Omega) = \sum_{m_1} e^{im(\alpha_1 - \phi_1 + \pi)} d_{mm_1}(\beta_1) e^{im_1(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi)} \\ \times d_{m_1 m'}(\beta_2) e^{im'(\alpha_2 + \beta_2)}, \quad (13)$$

with $m=0, m', m_1=0, \pm 1$ for a tensor of rank 1 (i.e., $l=1$), and $m=0, m', m_1=0, \pm 1, \pm 2$ for a tensor of rank 2 (i.e., $l=2$). Employing the above expressions and definitions, the $\alpha_{lm}(t)$ coefficients described in Eq. (9) are obtained by evaluating the $D_{mm'}(\Omega)$ coefficients. Since the transformation involving the rf pulses in NMR is often cyclic (with a time period $t_p = 2\pi/\omega_p$), the time-dependent $\alpha_{lm}(t)$ coefficients can be reexpressed in a compact form via the Fourier expansion,

$$\alpha_{lm}(t) = \sum_{k=-\infty}^{\infty} \alpha_{lmk} e^{ik\omega t}, \quad (14)$$

with α_{lmk} representing the time-independent Fourier coefficients corresponding to the Fourier index k . Depending on the rank of the tensor, the number of nonzero Fourier coefficients α_{lmk} vary in the above expression; a few of which we examine below.

Case I. For a tensor of rank 1 ($l=1, m=0$)

$$\alpha_{10\pm 2} = \left[\frac{1}{4} + \frac{1}{4} \cos(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi) \right], \quad (15)$$

$$\alpha_{100} = \left[\frac{1}{2} - \frac{1}{2} \cos(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi) \right].$$

Case II. For a tensor of rank 2 ($l=2, m=0$)

$$\alpha_{200} = \left[\frac{11}{32} - \frac{3}{8} \cos(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi) + \frac{9}{32} \cos(2(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi)) \right],$$

$$\alpha_{20\pm 2} = \left[\frac{6}{32} - \frac{6}{32} \cos(2(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi)) \right], \quad (16)$$

$$\alpha_{20\pm 4} = \left[\frac{9}{64} + \frac{3}{16} \cos(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi) + \frac{3}{64} \cos(2(\alpha_1 + \alpha_2 + \phi_1 - \phi_2 + \pi)) \right].$$

Employing the same procedure, other nonzero coefficients can be derived from Eq. (13) [i.e., $\alpha_{1\pm 1k}(k=\pm 1, \pm 2)$, $\alpha_{2\pm 1k}(k=\pm 1, \pm 2, \pm 3, \pm 4)$, $\alpha_{2\pm 2k}(k=0, \pm 1, \pm 2, \pm 3, \pm 4)$]. To highlight the differences between the performances of the various decoupling schemes and also to understand the relationship between the phase and amplitude of the rf pulses, the rf irradiation employed in the description is assumed to be cyclic and periodic. Under this approximation, CW decoupling is treated as a set of rf pulses with a constant phase while the XiX scheme is represented by a set of pulses whose phases differ by 180° . The performances of the various decoupling schemes depend on the α_{lmk} coefficients, a few of which are tabulated in Table I for the purposes of illustration. Employing the multipole operator basis (described in Table II), the time-dependent spin Hamiltonian in the rf interaction frame is represented by

TABLE I. α_{lmk} coefficients for various decoupling schemes. The phases of the two pulses (a) are identical (similar to CW decoupling), (b) are opposite (TPPM), (c) differ by 180° (XiX).

	α_{100}	$\alpha_{10\pm 2}$	α_{200}	$\alpha_{20\pm 2}$
(a) $\phi_1 = \phi_2$	0.178	0.41	0.05	0.21
(b) $\phi_1 = -\phi_2$	0.75	0.125	0.39	0.28
(c) $\phi_1 - \phi_2 = 180^\circ$	0.821	0.09	0.53	0.21

$$\tilde{H}(t) = \tilde{H}_S + \tilde{H}_I + \tilde{H}_{IS}, \quad (17)$$

where the interactions involving the S spins, represented by $\tilde{H}_S(t)$ are rendered time dependent only due to MAS,

$$\tilde{H}_S(t) = i g_0^{(3)} T_{\{0\}}^{(1)0}(001) + \sum_{\substack{m=-2 \\ m \neq 0}}^2 i G_m^{(3)} e^{im\omega_r t} T_{\{0\}}^{(1)0}(001). \quad (18)$$

The terms $g_0^{(3)}$ and $G_m^{(3)}$ represent the isotropic chemical shift and anisotropy of spin 3 (denoted by the superscript), respectively.

The spin interactions involving the I spins are represented by

$$\begin{aligned} \tilde{H}_I(t) = & \sum_{\substack{m=-2 \\ m \neq 0}}^2 \sum_{q=-1}^1 \sum_{k=-2}^2 \underbrace{\alpha_{1qk} e^{ik\omega_p t} (G_m^{(1)} e^{im\omega_r t} + g_0^{(1)}) i T_{\{1\}}^{(1)q}(100)}_{spin-1} + \sum_{\substack{m=-2 \\ m \neq 0}}^2 \sum_{q=-1}^1 \sum_{k=0, \pm 2}^2 \underbrace{\alpha_{1qk} e^{ik\omega_p t} (G_m^{(2)} e^{im\omega_r t} + g_0^{(2)}) i T_{\{1\}}^{(1)q}(010)}_{spin-2} \\ & + \sum_{\substack{m=-2 \\ m \neq 0}}^2 \sum_{q=-2}^2 \sum_{k=4}^{-4} \underbrace{G_m^{(12)} \alpha_{2qk} e^{im\omega_r t} e^{ik\omega_p t} T_{\{2\}}^{(2)q}(110)}_{spins-1,2} + \underbrace{J_{12} T_{\{0\}}^{(0)0}(110)}_{spins-1,2} \end{aligned} \quad (19)$$

where the isotropic chemical shift ($g_0^{(i)}$) is time dependent due to rf irradiation, while the CSA interaction ($G_m^{(i)}$) and the homonuclear dipolar interactions are time dependent both due to MAS as well as rf irradiation. The scalar coupling remains unaffected under both MAS as well as the rf irradiation.

The heteronuclear spin interactions are represented by \tilde{H}_{IS} ,

$$\begin{aligned} \tilde{H}_{IS}(t) = & \sum_{\substack{m=-2 \\ m \neq 0}}^2 \sum_{k=0, \pm 2}^2 \underbrace{\alpha_{10k} [G_m^{13,0} T_{\{1\}}^{(0)0}(101) + G_m^{13,2} T_{\{1\}}^{(2)0}(101) + G_m^{23,0} T_{\{1\}}^{(0)0}(011) + G_m^{23,2} T_{\{1\}}^{(2)0}(011)]}_{spins-1,3} e^{im\omega_r t} e^{ik\omega_p t} \\ & + \sum_{\substack{m=-2 \\ m \neq 0}}^2 \sum_{q_1=\pm 1}^2 \sum_{k=-2}^2 \underbrace{\alpha_{1q_1 k} [G_m^{13,1} T_{\{1\}}^{(1)q_1}(101) + G_m^{13,2} T_{\{1\}}^{(2)q_1}(101) + G_m^{23,1} T_{\{1\}}^{(1)q_1}(011) + G_m^{23,2} T_{\{1\}}^{(2)q_1}(011)]}_{spins-1,3} e^{im\omega_r t} e^{ik\omega_p t} \\ & + \underbrace{J_{13} T_{\{1\}}^{(0)0}(101)}_{spins-1,3} + \underbrace{J_{23} T_{\{1\}}^{(0)0}(011)}_{spins-2,3}, \end{aligned} \quad (20)$$

with the coefficients $G_m^{ij,0}$, $G_m^{ij,1}$, $G_m^{ij,2}$ associated with a particular spin pair (i, j) differing only by a numerical constant.

A. Floquet Hamiltonian

Employing the Floquet theorem and Shirley's procedure,³⁴ the time-dependent Hamiltonian in the rf interaction frame [Eq. (17)] is transformed into a time-independent Hamiltonian using a set of operators defined in an infinite dimensional basis set.

Such an approach provides an alternate theoretical description of multiple-pulse MAS experiments under asynchronous time modulations, as opposed to the traditional average Hamiltonian approach (or AHT), which requires the time modulations to be synchronized and fails to explain experimental phenomena when the various time averaging processes occur at competing time scales. Since the decoupling experiments described here involve two time modulations (namely, the sample spinning frequency and the applied rf field), the Hamiltonian is well described in a bimodal Floquet–Liouville space. Employing the multipole operator basis and Fourier operators,^{42,43} the Floquet Hamiltonian (denoted by H_F) for a three-spin system is represented by

$$H_F = H_0 + H_1. \quad (21)$$

The term H_0 refers to the zero-order Hamiltonian and involves operators, which are diagonal both in the spin (i.e., $q=0$) as well as in the Fourier dimension (i.e., $m=0, k=0$), and includes the time-independent scaled isotropic chemical shifts as well as the J -coupling interaction coefficients,

$$H_0 = \omega_r N^r + \omega_p N^p + i g_{00,0}^{(1)} T_{\{1\}}^{(1)0}(100) F_0^r F_0^p + i g_{00,0}^{(2)} T_{\{1\}}^{(1)0}(010) F_0^r F_0^p + i g_{00,0}^{(3)} T_{\{0\}}^{(1)0}(001) F_0^r F_0^p. \quad (22)$$

The operators N^r (associated with the rotor modulation) and N^p (associated with the rf modulation) connect Floquet states which are diagonal in the spin as well as in the Fourier dimension. The Fourier operators F_0^r and F_0^p are independent and connect states which are diagonal in their own respective domains. In the above expression, the notation $g_{0k,q}^{(i)}$

$= g_0^{(i)} \alpha_{1qk}$ has been employed and will be closely followed through the rest of this paper. The interaction term H_1 represents the perturbation involving operators which are off-diagonal both in the spin as well as in the Fourier dimension described below:

$$H_1 = H_{I(S)} + H_{II} + H_{IS}. \quad (23)$$

The chemical shift interactions (both isotropic as well as anisotropic) are represented by $H_{I(S)}$,

$$H_{I(S)} = \sum_{m,k,q} i(g_{0k,q}^{(1)} F_0^r F_k^p + G_{mk,q}^{(1)} F_m^r F_k^p) T_{\{1\}}^{(1)q}(100) + \sum_{m,k,q} i(g_{0k,q}^{(2)} F_0^r F_k^p + G_{mk,q}^{(2)} F_m^r F_k^p) T_{\{1\}}^{(1)q}(010) + \sum_m i G_{m0,0}^{(3)} T_{\{0\}}^{(1)0}(001) F_m^r F_0^p. \quad (24)$$

In the above expressions, the notation $G_{mk,q} = G_m \alpha_{1qk}$ has been employed with the summation indices, $m = \pm 1, \pm 2, k = 0, \pm 1, \pm 2, q = 0, \pm 1$. Since the zero-order Hamiltonian involves coefficients whose Fourier indices are zero, the Fourier indices (e.g., m, k, q) in the perturbing Hamiltonians cannot be equal to zero simultaneously.

The homonuclear dipolar interactions among the protons are represented by H_{II} ,

$$H_{II} = \sum_{m,k,q} G_{mk,q}^{12} T_{\{2\}}^{(2)q}(110) F_m^r F_k^p, \quad (25)$$

where $m = \pm 1, \pm 2, k = 0, \pm 1, \pm 2, \pm 4, q = 0, \pm 1, \pm 2$. The heteronuclear dipolar interactions (between the two protons and the carbon nuclei) are represented by H_{IS} ,

TABLE II. Operator basis for a three-spin system.

Operator basis	Classification	Number of operators
1. No spin		
$T_{\{0\}}^{(0)0}(000)$	Identity	1
2. Single-spin operators		
$T_{\{1\}}^{(1)q}(100)$	Spin 1 (proton)	3
$T_{\{1\}}^{(1)q}(010)$	Spin 2 (proton)	3
$T_{\{0\}}^{(1)q}(001)$	Spin 3 (carbon)	3
3. Two-spin operators		
$T_{\{2\}}^{(2)q}(110), T_{\{1\}}^{(1)q}(110), T_{\{0\}}^{(0)0}(110)$	Homonuclear interactions involving spin 1 and spin 2 (protons only)	5+3+1=9
$T_{\{1\}}^{(2)q}(101), T_{\{1\}}^{(1)q}(101), T_{\{1\}}^{(0)0}(101)$	Heteronuclear interactions involving spin 1 and spin 3.	5+3+1=9
$T_{\{1\}}^{(2)q}(011), T_{\{1\}}^{(1)q}(011), T_{\{1\}}^{(0)0}(011)$	Heteronuclear interactions involving spin 2 and spin 3.	5+3+1=9
4. Three-spin operators		
$T_{\{2\}}^{(3)q}(111), T_{\{2\}}^{(2)q}(111), T_{\{2\}}^{(1)q}(111)$		7+5+3=15
$T_{\{1\}}^{(2)q}(111), T_{\{1\}}^{(1)q}(111), T_{\{1\}}^{(0)0}(111)$		5+3+1=9
$T_{\{0\}}^{(1)q}(111)$		3
	Total	64

$$\begin{aligned}
H_{IS} = & \sum_{m,k} F_m^r F_k^p [G_{mk,0}^{13,0} T_{\{1\}}^{(0)0}(101) + G_{mk,0}^{13,2} T_{\{1\}}^{(2)0}(101)] \\
& + \sum_{m,k,q_1} F_m^r F_k^p [G_{mk,q_1}^{13,1} T_{\{1\}}^{(1)q_1}(101) + G_{mk,q_1}^{13,2} T_{\{1\}}^{(2)q_1}(101)] \\
& + \sum_{m,k} F_m^r F_k^p [G_{mk,0}^{23,0} T_{\{1\}}^{(0)0}(011) + G_{mk,0}^{23,2} T_{\{1\}}^{(2)0}(011)] \\
& + \sum_{m,k,q_1} F_m^r F_k^p [G_{mk,q_1}^{23,1} T_{\{1\}}^{(1)q_1}(011) \\
& + G_{mk,q_1}^{23,2} T_{\{1\}}^{(2)q_1}(011)], \quad (26)
\end{aligned}$$

where $m = \pm 1, \pm 2, k = 0, \pm 2$ and for $q_1 = \pm 1, k = \pm 1, \pm 2$.

In order to study the time-evolution of the system, the above Floquet Hamiltonian needs to be diagonalized. Since the Hamiltonian is highly off-diagonal and is described in an infinite-dimensional basis set, the standard approach often involves the numerical diagonalization of a truncated Floquet-Hamiltonian matrix. Though such numerical methods are robust, they often obscure analytical insights into the dynamics problem. This motivates the development of analytical methods based on perturbation theory for diagonalizing the Floquet-Hamiltonian matrix. In the following section we describe the utility of the van Vleck (or contact) transformation method for obtaining effective Floquet Hamiltonians.

B. Effective Floquet Hamiltonians via contact transformation method

The van Vleck or contact transformation method is an operator equivalent of the traditional Rayleigh-Schrödinger perturbation theory in which perturbation corrections take the form of operators, thereby leading to effective Hamiltonians. This approach has been described in detail by various researchers^{14,44} and will not be described in detail here. In this approach, the Floquet Hamiltonian is first split into a zero order and a perturbing term [illustrated in Eqs. (22) and (23), respectively], and then subjected to a unitary transformation represented below:

$$\begin{aligned}
H_F^{eff} &= U_1 H_F U_1^{-1} \\
&= e^{i\lambda S_1} H_F e^{-i\lambda S_1} \\
&= H_0^{(1)} + H_1^{(1)} + H_2^{(1)} + \dots, \\
H_0^{(1)} &= H_0, \\
H_1^{(1)} &= H_1 + i[S_1, H_0], \\
H_2^{(1)} &= H_2 + i[S_1, H_1] - \frac{1}{2}[S_1, [S_1, H_0]], \\
H_n^{(1)} &= H_n + \sum_{m=0}^{n-1} \frac{i^{n-m}}{(n-m)!} \underbrace{[S_1, [S_1 \dots [S_1, H_m] \dots]]}_{n-m} \quad (27)
\end{aligned}$$

In this new frame, the perturbation corrections to the zero-order Hamiltonian are obtained by proper choice of the trans-

formation function S_1 , which is usually expressed by a linear combination of the spin operators employed in the description of the perturbing Hamiltonian H_1 ,

$$\begin{aligned}
S_1 = & i[i(C_{0k,q}^{(1)} + C_{mk,q}^{(1)} F_m^r) F_k^p T_{\{1\}}^{(1)q}(100) + i(C_{0k,q}^{(2)} \\
& + C_{mk,q}^{(2)} F_m^r) F_k^p T_{\{1\}}^{(1)q}(010) + iC_{m0,0}^{(3)} F_m^r F_0^p T_{\{0\}}^{(1)0}(001) \\
& + C_{mk,q}^{12} F_m^r F_k^p T_{\{2\}}^{(2)q}(110) + C_{mk,q_1}^{23,2} F_m^r F_k^p T_{\{1\}}^{(2)q_1}(011) \\
& + C_{mk,q_1}^{23,1} F_m^r F_k^p T_{\{1\}}^{(1)q_1}(011) + C_{mk,0}^{23,2} F_m^r F_k^p T_{\{1\}}^{(2)0}(011) \\
& + C_{mk,0}^{23,0} F_m^r F_k^p T_{\{1\}}^{(0)0}(011) + C_{mk,q_1}^{13,2} F_m^r F_k^p T_{\{1\}}^{(2)q_1}(101) \\
& + C_{mk,q_1}^{13,1} F_m^r F_k^p T_{\{1\}}^{(1)q_1}(101) + C_{mk,0}^{13,2} F_m^r F_k^p T_{\{1\}}^{(2)0}(101) \\
& + C_{mk,0}^{13,0} F_m^r F_k^p T_{\{1\}}^{(0)0}(101)]. \quad (28)
\end{aligned}$$

Since the perturbing Hamiltonian H_1 is off-diagonal (both in the spin as well as Fourier space), the transformation function S_1 has to be off-diagonal in order to compensate the off-diagonality in H_1 (i.e., $[S_1, H_0]$ is off-diagonal). The C coefficients involved in the transformation function corresponding to a particular operator are chosen to compensate the corresponding off-diagonal terms in the perturbing Hamiltonian H_1 and are obtained by solving the following equation:

$$H_1^{(1)} = H_1 + i[S_1, H_0]. \quad (29)$$

The details involved are given in the previous paper¹ and have been described briefly in the Appendix. The coefficients involved in the transformation function are tabulated in Table III.

It is important to realize here that the commutator relation $[S_1, H_0]$, in addition to removing the off-diagonal character in H_1 (to certain order), also leads to other residual off-diagonal terms (i.e., $H_1^{(1)} \neq 0$), which depending on its relative magnitude to that of the zero-order Hamiltonian can be retained or neglected in further calculations,

$$\begin{aligned}
H_1^{(1)} = & \left[\frac{1}{\sqrt{6}} C_{mk,0}^{13,2} (g_{00,0}^{(3)} + g_{00,0}^{(1)}) + \frac{1}{\sqrt{6}} C_{mk,0}^{13,0} (g_{00,0}^{(3)} \right. \\
& \left. - g_{00,0}^{(1)}) \right] F_m^r F_k^p T_{\{1\}}^{(1)0}(101) + \left[\frac{1}{\sqrt{6}} C_{mk,0}^{23,2} (g_{00,0}^{(3)} + g_{00,0}^{(1)}) \right. \\
& \left. + \frac{1}{\sqrt{6}} C_{mk,0}^{23,0} (g_{00,0}^{(3)} - g_{00,0}^{(1)}) \right] F_m^r F_k^p T_{\{1\}}^{(1)0}(011) \\
& - \frac{\sqrt{4-q^2}}{2\sqrt{6}} C_{mk,q}^{12} (g_{00,0}^{(1)} - g_{00,0}^{(2)}) F_m^r F_k^p T_{\{1\}}^{(1)q}(110). \quad (30)
\end{aligned}$$

For the sake of simplicity, the following notation will be employed for describing the coefficients involved in Eq. (30),

TABLE III. Coefficients involved in the transformation function S_1 .

$$\begin{aligned}
C_{0k,q}^{(1)} &= \frac{g_{0k,q}^{(1)}}{k\omega_1 + \frac{q}{\sqrt{2}}g_{00,0}^{(1)}}, \\
C_{mk,q}^{(1)} &= \frac{G_{0k,q}^{(1)}}{m\omega_r + k\omega_1 + \frac{q}{\sqrt{2}}g_{00,0}^{(1)}}, \\
C_{0k,q}^{(2)} &= \frac{g_{0k,q}^{(2)}}{k\omega_1 + \frac{q}{\sqrt{2}}g_{00,0}^{(2)}}, \\
C_{mk,q}^{(2)} &= \frac{G_{0k,q}^{(2)}}{m\omega_r + k\omega_1 + \frac{q}{\sqrt{2}}g_{00,0}^{(2)}}, \\
C_{m0,0}^{(3)} &= \frac{G_{m0,0}^{(3)}}{m\omega_r}, \\
C_{mk,q}^{12} &= \frac{G_{mk,q}^{12}}{m\omega_r + k\omega_1 + \frac{q}{2\sqrt{2}}(g_{00,0}^{(1)} + g_{00,0}^{(2)})}, \\
C_{mk,0}^{13,2} &= \frac{G_{mk,0}^{13,2}}{m\omega_r + k\omega_1}, \quad C_{mk,0}^{13,0} = \frac{G_{mk,0}^{13,0}}{m\omega_r + k\omega_1}, \\
C_{mk,0}^{23,2} &= \frac{G_{mk,0}^{23,2}}{m\omega_r + k\omega_1}, \quad C_{mk,0}^{23,0} = \frac{G_{mk,0}^{23,0}}{m\omega_r + k\omega_1}, \\
C_{mk,q_1}^{13,1} &= \frac{\frac{1}{2\sqrt{2}}G_{mk,q_1}^{13,2} - a_1 G_{mk,q_1}^{13,1}}{\frac{1}{8\sqrt{3}} - a_1^2}, \\
C_{mk,q_1}^{13,2} &= \frac{\frac{1}{2\sqrt{6}}G_{mk,q_1}^{13,1} - a_1 G_{mk,q_1}^{13,2}}{\frac{1}{8\sqrt{3}} - a_1^2}, \\
C_{mk,q_1}^{23,1} &= \frac{\frac{1}{2\sqrt{2}}G_{mk,q_1}^{23,2} - a_1 G_{mk,q_1}^{23,1}}{\frac{1}{8\sqrt{3}} - a_1^2}, \\
C_{mk,q_1}^{23,2} &= \frac{\frac{1}{2\sqrt{6}}G_{mk,q_1}^{23,1} - a_1 G_{mk,q_1}^{23,2}}{\frac{1}{8\sqrt{3}} - a_1^2},
\end{aligned}$$

where $a_1 = m\omega_r + k\omega_1 - \frac{q}{2\sqrt{2}}$.

$$\begin{aligned}
H_1^{(1)} &= L_{mk,q}^{12} T_{\{1\}}^{(1)q}(110) F_m^r F_k^p + L_{mk,0}^{13} T_{\{1\}}^{(1)0}(101) F_m^r F_k^p \\
&\quad + L_{mk,0}^{23} T_{\{1\}}^{(1)0}(011) F_m^r F_k^p.
\end{aligned} \quad (31)$$

The second-order (or diagonal) corrections to the zero-order

Floquet Hamiltonian are obtained by evaluating Eq. (32),

$$\begin{aligned}
H_2^{(1)} &= H_2 + i[S_1, H_1] - \frac{1}{2}[S_1, [S_1, H_0]] \\
&= \frac{i}{2}[S_1, H_1] + \frac{i}{2}[S_1, H_1^{(1)}].
\end{aligned} \quad (32)$$

Following the procedure described in the previous paper,⁴⁰ the second-order corrections to the zero-order Hamiltonian can further be classified into three main categories described below:

$$H_2^{(1)} = H_{(\text{single spin})} + H_{(\text{Two spin})} + H_{(\text{Three spin})}. \quad (33)$$

The term $H_{(\text{single spin})}$ represents corrections to the single spin operators employed for spin description:

$$\begin{aligned}
H_{(\text{single spin})} &= [iA_{\{1\}}^{(1)0}(100)T_{\{1\}}^{(1)0}(100) \\
&\quad + iA_{\{1\}}^{(1)0}(010)T_{\{1\}}^{(1)0}(010) \\
&\quad + iA_{\{0\}}^{(1)0}(001)T_{\{0\}}^{(1)0}(001)]F_0^r F_0^p.
\end{aligned} \quad (34)$$

In order to understand the performance of the decoupling sequences, it is necessary to evaluate the exact contributions to the individual spin polarizations present in the model system (in this case, the observed nuclei and the two protons). The homonuclear dipolar interactions among the protons effectively reduce the spin polarization on the individual protons present in the system, thereby minimizing the residual heteronuclear dipolar interactions between the individual protons and the observed nuclei. This fact may be verified by the presence of the cross terms between the homonuclear dipolar interaction terms in the A coefficients (i.e., $A_{\{1\}}^{(1)0}(100)$, $A_{\{1\}}^{(1)0}(010)$), which represent corrections to the individual proton polarizations present in the model system. With an increase in the magnitude of the homonuclear dipolar interactions (among the protons), the spin polarization on the individual protons decreases significantly, thereby minimizing the residual heteronuclear dipolar interaction. Subsequently, this enhances the performance of a particular decoupling scheme. In addition to the dependence on the homonuclear dipolar interactions, the proton spin polarization also depends on the cross terms between the heteronuclear dipolar interaction terms as well as the chemical shift interaction terms (which include the CSA and scaled isotropic shift). These are illustrated in Table IV. Such cross terms have never been reported in previous theoretical treatments of the decoupling phenomenon. The spin polarization on the observed nuclei (represented by $A_{\{0\}}^{(1)0}(001)$) involves cross terms between the various heteronuclear dipolar interaction terms (between the two protons and the observed nuclei).

The cross terms between the various anisotropic interactions are represented by two-spin ($H_{(\text{Two spin})}$) and three-spin terms ($H_{(\text{Three spin})}$) in the Hamiltonian. The two-spin corrections are obtained from cross terms between the dipolar interactions and the chemical shift interactions and are represented below:

TABLE IV. Second-order corrections involving single-spin operators.

$A_{(1)}^{(1)0} (100)$	$\frac{q_1(-1)^{q_1}}{4\sqrt{2}} \left[\underbrace{C_{mk,q_1}^{12} G_{-m-k,-q_1}^{12}}_{\text{dipole-dipole(spins 1&2)}} - \frac{q_2}{2\sqrt{2}} \left[\underbrace{C_{mk,q_2}^{(1)} G_{-m-k,-q_2}^{(1)} + C_{0k,q_2}^{(1)} G_{0-k,-q_2}^{(1)}}_{\text{csa-csa}} \right] \right.$ $- \frac{(-1)^{q_2} \sqrt{4-q_2^2}}{4\sqrt{6}} \left[\underbrace{C_{mk,q_2}^{12} L_{-m-k,-q_2}^{12}}_{\text{dipole-dipole(spins 1&2)}} + \frac{q_3}{4\sqrt{2}} \left[\underbrace{C_{mk,q_3}^{13,1} G_{-m-k,-q_3}^{13,1} - C_{mk,q_3}^{13,2} G_{-m-k,-q_3}^{13,2}}_{\text{dipole-dipole(spins 1&3)}} \right] + \right.$ $\left. \frac{\sqrt{4-q_3^2}}{4\sqrt{6}} \left[\underbrace{C_{mk,q_3}^{13,2} G_{-m-k,-q_3}^{13,1} - C_{mk,-q_3}^{13,1} G_{-m-k,q_3}^{13,2}}_{\text{dipole-dipole(spins 1&3)}} \right] + \frac{1}{2\sqrt{3}} \left[\underbrace{C_{mk,0}^{13,0} L_{-m-k,0}^{13,1} - \frac{1}{\sqrt{2}} C_{mk,0}^{13,2} L_{-m-k,0}^{13,1}}_{\text{sdipole-dipole(spins 1&3)}} \right] \right.$ <p style="text-align: center;">where $q_1 = 0, \pm 1, \pm 2$ $q_2 = 0, \pm 1$ $q_3 = \pm 1$</p>
$A_{(1)}^{(1)0} (010)$	$\frac{q_1(-1)^{q_1}}{4\sqrt{2}} \left[\underbrace{C_{mk,q_1}^{12} G_{-m-k,-q_1}^{12}}_{\text{dipole-dipole(spins 1&2)}} - \frac{q_2}{2\sqrt{2}} \left[\underbrace{C_{mk,q_2}^{(2)} G_{-m-k,-q_2}^{(2)} + C_{0k,q_2}^{(2)} G_{0-k,-q_2}^{(2)}}_{\text{csa-csa}} \right] \right.$ $+ \frac{(-1)^{q_2} \sqrt{4-q_2^2}}{4\sqrt{6}} \left[\underbrace{C_{mk,q_2}^{12} L_{-m-k,-q_2}^{12}}_{\text{dipole-dipole(spins 1&2)}} + \frac{q_3}{4\sqrt{2}} \left[\underbrace{C_{mk,q_3}^{23,1} G_{-m-k,-q_3}^{23,1} - C_{mk,q_3}^{23,2} G_{-m-k,-q_3}^{23,2}}_{\text{dipole-dipole(spins 2&3)}} \right] + \right.$ $\left. \frac{\sqrt{4-q_3^2}}{4\sqrt{6}} \left[\underbrace{C_{mk,q_3}^{23,2} G_{-m-k,-q_3}^{23,1} - C_{mk,-q_3}^{23,1} G_{-m-k,q_3}^{23,2}}_{\text{dipole-dipole(spins 2&3)}} \right] + \frac{1}{2\sqrt{3}} \left[\underbrace{C_{mk,0}^{23,0} L_{-m-k,0}^{23,1} - \frac{1}{\sqrt{2}} C_{mk,0}^{23,2} L_{-m-k,0}^{23,1}}_{\text{dipole-dipole(spins 2&3)}} \right] \right.$ <p style="text-align: center;">where $q_1 = 0, \pm 1, \pm 2$ $q_2 = 0, \pm 1$ $q_3 = \pm 1$</p>
$A_{(1)}^{(1)0} (001)$	$\frac{q_3}{4\sqrt{2}} \left[\underbrace{C_{mk,q_3}^{13,1} G_{-m-k,-q_3}^{13,1} + C_{mk,q_3}^{23,1} G_{-m-k,-q_3}^{23,1} - C_{mk,q_3}^{13,2} G_{-m-k,-q_3}^{13,2} - C_{mk,q_3}^{23,2} G_{-m-k,-q_3}^{23,2}}_{\text{dipole-dipole(spins 1&3 and spins 2&3)}} \right] +$ $\frac{1}{4\sqrt{2}} \left[\underbrace{C_{mk,-q_3}^{13,1} G_{-m-k,q_3}^{13,2} - C_{mk,q_3}^{13,2} G_{-m-k,-q_3}^{13,1}}_{\text{dipole-dipole(spins 1&3)}} + \frac{1}{4\sqrt{2}} \left[\underbrace{C_{mk,-q_3}^{23,1} G_{-m-k,q_3}^{23,2} - C_{mk,q_3}^{23,2} G_{-m-k,-q_3}^{23,1}}_{\text{dipole-dipole(spins 2&3)}} \right] \right.$ $\left. \frac{1}{2\sqrt{6}} \left[\underbrace{C_{mk,0}^{13,2} L_{-m-k,0}^{13,1} + C_{mk,0}^{23,2} L_{-m-k,0}^{23,1}}_{\text{dipole-dipole(spins 1&3 and spins 2&3)}} \right] - \frac{1}{2\sqrt{3}} \left[\underbrace{C_{mk,0}^{13,0} L_{-m-k,0}^{13,1} + C_{mk,0}^{23,0} L_{-m-k,0}^{23,1}}_{\text{dipole-dipole(spins 1&3 and spins 2&3)}} \right] \right.$ <p style="text-align: center;">where $q_3 = \pm 1$</p>

$$\begin{aligned}
H(\text{Two spin}) = & [A_{\{2\}}^{(2)0}(110)T_{\{2\}}^{(2)0}(110) + A_{\{1\}}^{(1)0}(110)T_{\{1\}}^{(1)0}(110) \\
& + A_{\{0\}}^{(0)0}(110)T_{\{0\}}^{(0)0}(110) + A_{\{1\}}^{(2)0}(101)T_{\{1\}}^{(2)0}(101) \\
& + A_{\{1\}}^{(1)0}(101)T_{\{1\}}^{(1)0}(101) + A_{\{1\}}^{(0)0}(101)T_{\{1\}}^{(0)0}(101) \\
& + A_{\{1\}}^{(2)0}(011)T_{\{1\}}^{(2)0}(011) + A_{\{1\}}^{(1)0}(011)T_{\{1\}}^{(1)0}(011) \\
& + A_{\{1\}}^{(0)0}(011)T_{\{1\}}^{(0)0}(011)]F_0^r F_0^p, \quad (35)
\end{aligned}$$

wherein the first row represents the cross terms between the homonuclear dipolar interaction (among the protons) and the chemical shift interactions (of the two protons). The cross terms between the pairs of heteronuclear dipolar interactions (spins 1 and 3 and spins 2 and 3) and the chemical shift interactions are represented along the second and third rows, respectively, and have been tabulated in Table V.

The corrections to three-spin operators are represented by

$$\begin{aligned}
H(\text{Three spin}) = & [A_{\{2\}}^{(3)0}(110)T_{\{2\}}^{(3)0}(111) + A_{\{2\}}^{(2)0}(111)T_{\{2\}}^{(2)0}(111) \\
& + A_{\{2\}}^{(1)0}(111)T_{\{2\}}^{(1)0}(111) + A_{\{1\}}^{(2)0}(110)T_{\{1\}}^{(2)0}(111) \\
& + A_{\{1\}}^{(1)0}(111)T_{\{1\}}^{(1)0}(111) + A_{\{1\}}^{(0)0}(111)T_{\{1\}}^{(0)0}(111) \\
& + A_{\{0\}}^{(1)0}(111)T_{\{0\}}^{(1)0}(111)]F_0^r F_0^p. \quad (36)
\end{aligned}$$

Since the above expression involves three-spin operators, the corrections have to involve cross terms between the homonuclear dipolar interactions (involving spins 1 and 2) and heteronuclear dipolar interactions (involving spins 1 and 3 and spins 2 and 3) and have been tabulated in Table VI. The correction terms represented in Tables V and VI involve cross terms between the various anisotropic interactions present in the system and are responsible for the residual line broadening observed in the ^{13}C MAS spectrum. It is important to note that the correction terms illustrated above have been obtained using a set of relations among the Fourier operators described in the previous paper, in addition to the commutator relation for a three-spin system, given below:

TABLE V. Second-order corrections involving two spin operators.

$A_{(2)}^{(2)0} \text{ (110)}$	$-\frac{q_2\sqrt{4-q_2^2}}{4\sqrt{2}} \left[(C_{mk,q_2}^{(1)} + C_{mk,q_2}^{(2)}) G_{-m-k,-q_2}^{12} - C_{mk,-q_2}^{12} (G_{-m-k,q_2}^{(1)} + G_{-m-k,q_2}^{(2)}) \right] +$ $\frac{(-1)^{l-q_2} (3-q_2^2)}{4\sqrt{6}} \left[L_{-m-k,-q_2}^{12} (C_{mk,q_2}^{(1)} - C_{mk,q_2}^{(2)}) \right] \text{ where } q_2 = 0, \pm 1$ <p style="text-align: center;"><i>dipolar (spins 1&2)-CSA of spin 1 and 2</i></p>
$A_{(1)}^{(1)0} \text{ (110)}$	$\frac{\sqrt{4-q_2^2}}{4\sqrt{6}} \left\{ (C_{mk,q_2}^{(2)} - C_{mk,q_2}^{(1)}) G_{-m-k,-q_2}^{12} - C_{mk,-q_2}^{12} (G_{-m-k,q_2}^{(2)} - G_{-m-k,q_2}^{(1)}) \right\} +$ $\frac{q_2}{4\sqrt{2}} \left[L_{-m-k,-q_2}^{12} (C_{mk,q_2}^{(1)} + C_{mk,q_2}^{(2)}) \right] \text{ where } q_2 = 0, \pm 1$ <p style="text-align: center;"><i>dipolar (spins 1&2)-CSA of spin 1 and 2</i></p>
$A_{(0)}^{(0)0} \text{ (110)}$	$\frac{1}{2\sqrt{3}} \left[L_{-m-k,-q_2}^{12} (C_{mk,q_2}^{(1)} - C_{mk,q_2}^{(2)}) \right] \text{ where } q_2 = 0, \pm 1$ <p style="text-align: center;"><i>dipolar (spins 1&2)-CSA of spin 1 and 2</i></p>
$A_{(1)}^{(2)0} \text{ (101)}$	$-\frac{q_3\sqrt{4-q_3^2}}{4\sqrt{2}} \left\{ C_{mk,q_3}^{(1)} G_{-m-k,-q_3}^{13,2} - C_{mk,-q_3}^{13,2} G_{-m-k,q_3}^{(1)} \right\} +$ <p style="text-align: center;"><i>dipolar (1&3)-CSA of spin-1</i></p> $\left[\frac{1}{2\sqrt{6}} L_{-m-k,0}^{13} C_{mk,0}^{(1)} \right] - \left[\frac{1}{2\sqrt{6}} L_{-m,0}^{13} C_{m,0}^{(3)} \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;"><i>dipolar (1&3)-CSA of spin-1 dipolar (1&3)-CSA of spin-3</i></p>
$A_{(1)}^{(1)0} \text{ (101)}$	$-\frac{\sqrt{4-q_3^2}}{4\sqrt{6}} \left\{ C_{mk,q_3}^{(1)} G_{-m-k,-q_3}^{13,2} - C_{mk,-q_3}^{13,2} G_{-m-k,q_3}^{(1)} \right\} - \frac{1}{4} \left[L_{-m-k,0}^{13} C_{mk,0}^{(1)} \right]$ <p style="text-align: center;"><i>dipolar (1&3)-CSA of spin 1 dipolar (1&3)-CSA of spin 1</i></p> $-\frac{1}{2\sqrt{3}} \left[C_{m,0,0}^{(3)} (G_{-m,0,0}^{13,2} + G_{-m,0,0}^{13,0}) - G_{-m,0,0}^{(3)} (C_{m,0,0}^{13,2} + C_{m,0,0}^{13,0}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;"><i>dipolar (1&3)-CSA of spin-3</i></p>
$A_{(1)}^{(0)0} \text{ (101)}$	$\frac{1}{2\sqrt{3}} \left[L_{-m-k,0}^{13} C_{mk,0}^{(1)} \right] + \frac{1}{2\sqrt{3}} \left[L_{-m,0,0}^{13} C_{m,0,0}^{(3)} \right]$ <p style="text-align: center;"><i>dipolar (1&3)-CSA of spin 1 dipolar (1&3)-CSA of spin 3</i></p>
$A_{(0)}^{(2)0} \text{ (011)}$	$-\frac{q_3\sqrt{4-q_3^2}}{4\sqrt{2}} \left\{ C_{mk,q_3}^{(2)} G_{-m-k,-q_3}^{23,2} - C_{mk,-q_3}^{23,2} G_{-m-k,q_3}^{(2)} \right\} +$ <p style="text-align: center;"><i>dipolar (2&3)-CSA of spin 2</i></p> $\frac{1}{2\sqrt{6}} \left[L_{-m-k,0}^{23} C_{mk,0}^{(2)} - L_{-m,0,0}^{23} C_{m,0,0}^{(3)} \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;"><i>dipolar (2&3)-CSA of spin 2</i></p>
$A_{(1)}^{(1)0} \text{ (011)}$	$-\frac{\sqrt{4-q_3^2}}{4\sqrt{6}} \left\{ C_{mk,q_3}^{(2)} G_{-m-k,-q_3}^{23,2} - C_{mk,-q_3}^{23,2} G_{-m-k,q_3}^{(2)} \right\} - \frac{1}{4} \left[L_{-m-k,0}^{23} C_{mk,0}^{(2)} \right]$ <p style="text-align: center;"><i>dipolar (2&3)-CSA of spin -2 dipolar (2&3)-CSA of spin -2</i></p> $-\frac{1}{2\sqrt{3}} \left[C_{m,0,0}^{(3)} (G_{-m,0,0}^{23,2} + G_{-m,0,0}^{23,0}) - G_{-m,0,0}^{(3)} (C_{m,0,0}^{23,2} + C_{m,0,0}^{23,0}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;"><i>dipolar (2&3)-CSA of spin -3</i></p>
$A_{(1)}^{(0)0} \text{ (011)}$	$\frac{1}{2\sqrt{3}} \left[L_{-m-k,0}^{23} C_{mk,0}^{(2)} \right] + \frac{1}{2\sqrt{3}} \left[L_{-m,0,0}^{23} C_{m,0,0}^{(3)} \right]$ <p style="text-align: center;"><i>dipolar (2&3)-CSA of spin 2 dipolar (2&3)-CSA of spin 3</i></p>

TABLE VI. Second-order corrections involving three-spin operators.

$A_{(2)}^{(3)0} \text{ (111)}$	$\frac{q_3}{2\sqrt{5}} \left\{ (G_{-m-k,-q_3}^{13,2} + G_{-m-k,-q_3}^{23,2}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,2} + C_{mk,-q_3}^{23,2}) \right\} -$ $\frac{1}{4\sqrt{5}} \left\{ (G_{-m-k,-q_3}^{13,1} + G_{-m-k,-q_3}^{23,1}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,1} + C_{mk,-q_3}^{23,1}) \right\} -$ $\frac{1}{4\sqrt{5}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,2} - C_{-m-k,-q_3}^{23,2}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;">hom onuclear dipolar(1&2)-heteronuclear dipolar(1&3 and 2&3)</p>
$A_{(2)}^{(2)0} \text{ (111)}$	$\frac{1}{8\sqrt{2}} \left\{ (G_{-m-k,-q_3}^{13,2} + G_{-m-k,-q_3}^{23,2}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,2} + C_{mk,-q_3}^{23,2}) \right\} +$ $\frac{q_3}{8\sqrt{2}} \left\{ (G_{-m-k,-q_3}^{13,1} + G_{-m-k,-q_3}^{23,1}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,1} + C_{mk,-q_3}^{23,1}) \right\} +$ $\frac{q_3}{8\sqrt{2}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,2} - C_{-m-k,-q_3}^{23,2}) \right] - \frac{q_3}{8\sqrt{2}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,1} - C_{-m-k,-q_3}^{23,1}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;">hom onuclear dipolar(1&2)-heteronuclear dipolar(1&3 and 2&3)</p>
$A_{(2)}^{(1)0} \text{ (111)}$	$-\frac{3q_3}{8\sqrt{30}} \left\{ (G_{-m-k,-q_3}^{13,2} + G_{-m-k,-q_3}^{23,2}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,2} + C_{mk,-q_3}^{23,2}) \right\} +$ $\frac{9}{8\sqrt{30}} \left\{ (G_{-m-k,-q_3}^{13,1} + G_{-m-k,-q_3}^{23,1}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,1} + C_{mk,-q_3}^{23,1}) \right\} -$ $\frac{1}{8\sqrt{30}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,2} - C_{-m-k,-q_3}^{23,2}) \right] - \frac{5q_3}{4\sqrt{30}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,1} - C_{-m-k,-q_3}^{23,1}) \right]$ $-\frac{\sqrt{5}}{12} \left[L_{mk,0}^{12} (C_{-m-k,0}^{13,0} - C_{-m-k,0}^{23,0}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;">hom onuclear dipolar(1&2)-heteronuclear dipolar(1&3 and 2&3)</p>
$A_{(1)}^{(2)0} \text{ (111)}$	$-\frac{1}{8\sqrt{6}} \left\{ (G_{-m-k,-q_3}^{13,2} - G_{-m-k,-q_3}^{23,2}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,2} - C_{mk,-q_3}^{23,2}) \right\} +$ $\frac{q_3}{8\sqrt{2}} \left\{ (G_{-m-k,-q_3}^{13,1} - G_{-m-k,-q_3}^{23,1}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,1} - C_{mk,-q_3}^{23,1}) \right\} +$ $\frac{q_3\sqrt{3}}{8\sqrt{2}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,2} + C_{-m-k,-q_3}^{23,2}) \right] + \frac{1}{8\sqrt{6}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,1} + C_{-m-k,-q_3}^{23,1}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;">hom onuclear dipolar(1&2)-heteronuclear dipolar(1&3 and 2&3)</p>
$A_{(1)}^{(1)0} \text{ (111)}$	$\frac{q_3}{8\sqrt{2}} \left\{ (G_{-m-k,-q_3}^{13,2} - G_{-m-k,-q_3}^{23,2}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,2} - C_{mk,-q_3}^{23,2}) \right\} +$ $\frac{1}{8\sqrt{2}} \left\{ (G_{-m-k,-q_3}^{13,1} - G_{-m-k,-q_3}^{23,1}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,1} - C_{mk,-q_3}^{23,1}) \right\} -$ $\frac{1}{8\sqrt{2}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,2} + C_{-m-k,-q_3}^{23,2}) \right] + \frac{q_3}{8\sqrt{2}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,1} + C_{-m-k,-q_3}^{23,1}) \right]$ $\frac{1}{4\sqrt{3}} \left[L_{mk,0}^{12} (C_{-m-k,0}^{13,0} + C_{-m-k,0}^{23,0}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;">hom onuclear dipolar(1&2)-heteronuclear dipolar(1&3 and 2&3)</p>
$A_{(1)}^{(0)0} \text{ (111)}$	$\frac{1}{4\sqrt{3}} \left\{ (G_{-m-k,-q_3}^{13,2} - G_{-m-k,-q_3}^{23,2}) C_{mk,q_3}^{12} - G_{-m-k,q_3}^{12} (C_{mk,-q_3}^{13,2} - C_{mk,-q_3}^{23,2}) \right\} -$ $\frac{1}{4\sqrt{3}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,1} + C_{-m-k,-q_3}^{23,1}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;">hom onuclear dipolar(1&2)-heteronuclear dipolar(1&3 and 2&3)</p>
$A_{(1)}^{(1)0} \text{ (111)}$	$\frac{1}{2\sqrt{6}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,2} - C_{-m-k,-q_3}^{23,2}) \right] + \frac{q_3}{\sqrt{6}} \left[L_{mk,q_3}^{12} (C_{-m-k,-q_3}^{13,1} - C_{-m-k,-q_3}^{23,1}) \right]$ $+ \frac{1}{\sqrt{6}} \left[L_{mk,0}^{12} (C_{-m-k,0}^{13,0} - C_{-m-k,0}^{23,0}) \right] \text{ where } q_3 = \pm 1$ <p style="text-align: center;">hom onuclear dipolar(1&2)-heteronuclear dipolar(1&3 and 2&3)</p>

$$\begin{aligned}
[T_{L_1}^{(l)m}(l_1 l_2 l_3), T_{K_1}^{(k')q'}(k'_1 k'_2 k'_3)] = & \sum_{k''_1, k''_2, k''_3, K''_1, K''_2, K''_3, q''} 2\phi_{i=1 \rightarrow 3}(l_i k'_i k''_i) (-1)^{2(l_1+l_2+l_3)} \\
& \times (i)^{l_1+l_2+l_3} (i)^{k'_1+k'_2+k'_3} (i)^{k''_1+k''_2+k''_3} \\
& \times \sqrt{(2L_1+1)(2K_1'+1)(2K_1''+1)} \prod_{i=1}^3 (2l_i+1) \prod_{i=1}^3 (2k'_i+1) \prod_{i=1}^3 (2k''_i+1) \\
& \times \sqrt{(2l+1)(2k'+1)(2k''+1)} \begin{Bmatrix} k''_1 & l_1 & k'_1 \\ l_1 & l_1 & l_1 \end{Bmatrix} \begin{Bmatrix} k''_2 & l_2 & k'_2 \\ l_2 & l_2 & l_2 \end{Bmatrix} \begin{Bmatrix} k''_3 & l_3 & k'_3 \\ l_3 & l_3 & l_3 \end{Bmatrix} \\
& \times \begin{Bmatrix} l_1 & l_2 & L_1 \\ k'_1 & k'_2 & K_1' \end{Bmatrix} \begin{Bmatrix} L_1 & l_3 & l \\ K_1' & k'_3 & k' \end{Bmatrix} \begin{Bmatrix} l & k' & k'' \\ k''_1 & k''_2 & K_1'' \end{Bmatrix} \begin{Bmatrix} K_1'' & k''_3 & k'' \\ k''_1 & k''_2 & K_1'' \end{Bmatrix} (-1)^{k''-q''} \begin{pmatrix} l & k' & k'' \\ m & q' & -q'' \end{pmatrix} T_{K_1''}^{(k'')q''}(k''_1 k''_2 k''_3)
\end{aligned}$$

with $\phi_{i=1 \rightarrow 3}(l_i k'_i k''_i) = 1$ if $\sum_{i=1}^3 l_i + k'_i + k''_i = \text{odd}$
 $= 0$ (otherwise). (37)

The commutator expression described above has been generalized for N spins and has been explained in detail in earlier publications.³² Since the entire algebra is based on the theory of spin angular momentum, extensions to higher spin magnitudes and multiple spins are quite straightforward. This is in contrast to other existing theoretical methods, which often require multiple commutator expressions to be evaluated, a task which becomes quite tedious beyond two spins. Further, the symmetry embedded in the multipole basis aids in representation and evaluation of the correction terms, while other theoretical descriptions do not readily explain the origin of the various cross terms and their contributions in the spin dynamics.

The superior performance of multiple pulse decoupling schemes such as TPPM and XiX over CW decoupling can be explained using Eqs. (13)–(16) and has been tabulated in Table I using typical parameters employed in solid-state NMR.¹⁹ Several general features of a successful decoupling sequence are embedded in these relations. First, current approaches often neglect the effects of proton offsets in decoupling, which we believe leads to inaccurate interpretation of the decoupling phenomena in general. This aspect has been accounted for in our approach using Eq. (10). Next, any decoupling scheme should involve an active recoupling of the homonuclear dipolar interaction in addition to minimizing the cross terms between the various interactions present in the system. The former aids in effectively minimizing the spin polarization on the protons while the latter condition minimizes the residual line broadening observed in the ¹³C-MAS spectrum. The effective Hamiltonians derived in this approach clearly illustrate the role of homonuclear dipolar interactions among the protons in the better performance of the decoupling schemes. This fact is clearly illustrated in the coefficients involved in Eq. (34). In the case of CW decoupling, the homonuclear dipolar interactions are scaled to

a larger extent when compared to other decoupling schemes. This is responsible for its mediocre performance when compared with other decoupling schemes. Such effects become pronounced at higher spinning frequencies leading to the self-decoupling phenomenon observed experimentally by Meier *et al.* In the case of TPPM and XiX decoupling schemes, the scaling factor corresponding to the homonuclear dipolar interaction is high when compared to the CW decoupling scheme. However at higher spinning frequencies (greater than 20 kHz) and high rf field strengths, the XiX scheme should perform somewhat better than TPPM mainly due to the effective reduction of the homonuclear dipolar interactions at higher spinning frequencies in the case of TPPM decoupling. However, at low spinning frequencies and rf field strengths TPPM is superior to the XiX sequence mainly due to the reduced magnitude of the cross terms between the homonuclear dipolar and the heteronuclear dipolar interactions, which is in agreement with experimental results. These experimental observations are predicted using the theoretical approach presented in this paper.

A further unique prediction of this theory arises from the fact that three coupled spins have been treated, not only two. Observed discrepancies between theoretical predictions based on two-spin models and actual experimental observations in real solid systems have forced researchers to include the dense coupling among the protons in the spin dynamical model. The model three-spin system employed in our calculations, however, reveals other cross terms neglected in previous theoretical descriptions. To this end Ernst *et al.* proposed a model incorporating the effects of the strong homonuclear dipolar couplings into the two-spin model without increasing the complexity of the problem. In their approach, the dense coupling among the protons is described using a spin diffusion type relaxation operator described in the Liouville space.

The MMFT approach presented here can, in principle, treat the dense proton network quantum mechanically as a phenomenological spin system of higher spin magnitude (i.e., a proton spin bath involving 20 spins can be represented as a single spin system with spin magnitude $I=10$, if the internal configuration of the 20 spins can be neglected). Thus, the decoupling problem involving 16 protons ($I_{16}S$) can, in principle, be treated as a model two-spin system involving spins $I_1=1/2$ (representing carbon) and $I_2=8$ (representing the abundant spin bath) described in the Liouville space of dimension 1156×1156 . Since the entire spin dynamics described here involves the evaluation of a single commutator expression [given in Eq. (36)], which employs the well-known angular momentum algebra involving the Wigner-3J, -6J, -9J coefficients, extensions to higher spin magnitudes are quite straightforward and elegant for any analytical treatments beyond two spins. Work along these lines is currently in progress.

III. CONCLUSIONS

In summary, the effective Floquet Hamiltonians for a model three-spin system derived based on the MMFT approach aid in understanding the spin dynamics during heteronuclear decoupling in solid-state NMR. The use of such a model system aids in explaining the salient features observed during heteronuclear decoupling in addition to the performances of various decoupling schemes under MAS, even in cases where the time modulations corresponding to sample spinning and rf decoupling are asynchronous. In systems of multiple spins or higher spin magnitudes, analytical treatments based on Floquet theory are greatly simplified through a combination of the multipole basis, for spin description, and the van Vleck transformation, which yields analytical insights into the spin dynamics by means of an effective Hamiltonian. The analytical approach presented here is quite general, and we anticipate that it will be useful in a broad spectrum of problems in solid-state NMR. These applications will be illustrated with experiments and simulations in future publications.

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APPENDIX: EVALUATION OF S_1

The C coefficients involved in the transformation function S_1 can be evaluated by solving the equation given below:

$$H_1^{(1)} = H_1 + i[S_1, H_0]. \quad (\text{A1})$$

Since the main objective of the transformation function is to compensate the off-diagonality present in the perturbing Hamiltonian H_1 , the transformation function S_1 is chosen to be off-diagonal and is usually expressed as a linear combination of the operators involved in the perturbing Hamil-

tonian H_1 . The C coefficients are obtained by evaluating the commutator $[S_1, H_0]$, and equating the coefficients associated with a particular operator to zero. This is illustrated here as an example by evaluating the $C_{mk,q_1}^{13,1}$ and $C_{mk,q_1}^{13,2}$ coefficients, which are associated with the operators $T_{\{1\}}^{(1)q_1}(101)$ and $T_{\{1\}}^{(2)q_1}(101)$, respectively,

$$T_{\{1\}}^{(2)q_1}(101) \left[\left(G_{mk,q_1}^{13,2} - (m\omega_r + k\omega_1 - q/2\sqrt{2}) \right) C_{mk,q_1}^{13,2} - \frac{1}{2\sqrt{6}} C_{mk,q_1}^{13,1} \right] = 0, \quad (\text{A2})$$

$$T_{\{1\}}^{(1)q_1}(101) \left[\left(G_{mk,q_1}^{13,1} - (m\omega_r + k\omega_1 - q/2\sqrt{2}) \right) C_{mk,q_1}^{13,1} - \frac{1}{2\sqrt{2}} C_{mk,q_1}^{13,2} \right] = 0. \quad (\text{A3})$$

These two equations form a set of coupled equations, with the C coefficients being the unknowns, which, however, can be obtained by solving the above linear equations. The other C coefficients mainly involve simple linear equations of the type $aC+b=0$, where a and b are constant coefficients.

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