

Effective Floquet Hamiltonians for dipolar and quadrupolar coupled N-spin systems in solid state nuclear magnetic resonance under magic angle spinning

Manoj Kumar Pandey and Mangala Sunder Krishnan

Citation: *The Journal of Chemical Physics* **133**, 174121 (2010); doi: 10.1063/1.3496407

View online: <http://dx.doi.org/10.1063/1.3496407>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/133/17?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Zero-quantum stochastic dipolar recoupling in solid state nuclear magnetic resonance](#)

J. Chem. Phys. **137**, 104201 (2012); 10.1063/1.4749258

[Recoupling of native homonuclear dipolar couplings in magic-angle-spinning solid-state NMR by the double-oscillating field technique](#)

J. Chem. Phys. **133**, 064501 (2010); 10.1063/1.3464334

[Heteronuclear dipolar recoupling in solid-state nuclear magnetic resonance by amplitude-, phase-, and frequency-modulated Lee–Goldburg cross-polarization](#)

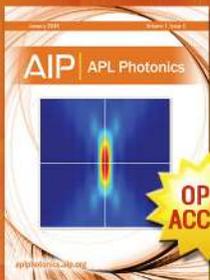
J. Chem. Phys. **122**, 044512 (2005); 10.1063/1.1834569

[Second order average Hamiltonian theory of symmetry-based pulse schemes in the nuclear magnetic resonance of rotating solids: Application to triple-quantum dipolar recoupling](#)

J. Chem. Phys. **120**, 11726 (2004); 10.1063/1.1738102

[Residual dipolar coupling in the CP/MAS nuclear magnetic resonance spectra of spin-1/2 nuclei coupled to quadrupolar nuclei application of floquet theory](#)

J. Chem. Phys. **116**, 2464 (2002); 10.1063/1.1433003



Launching in 2016!
The future of applied photonics research is here

OPEN ACCESS

AIP | APL
Photonics

Effective Floquet Hamiltonians for dipolar and quadrupolar coupled N-spin systems in solid state nuclear magnetic resonance under magic angle spinning

Manoj Kumar Pandey and Mangala Sunder Krishnan^{a)}

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

(Received 5 April 2010; accepted 13 September 2010; published online 4 November 2010)

Spin dynamics under magic angle spinning has been studied using different theoretical approaches and also by extensive numerical simulation programs. In this article we present a general theoretical approach that leads to analytic forms for effective Hamiltonians for an N-spin dipolar and quadrupolar coupled system under magic angle spinning (MAS) conditions, using a combination of Floquet theory and van Vleck (contact) transformation. The analytic forms presented are shown to be useful for the study of MAS spin dynamics in solids with the help of a number of simulations in two, three, and four coupled, spin-1/2 systems as well as spins in which quadrupolar interactions are also present. © 2010 American Institute of Physics. [doi:10.1063/1.3496407]

I. INTRODUCTION

Advances in nuclear magnetic resonance (NMR) spectroscopy in the last several decades have led to a variety of simulation programs and techniques for following the dynamics of nuclear spins in external magnetic fields as well as those which are inherently due to the electronic and magnetic environment surrounding the nuclei.¹ Many novel pulse schemes and multidimensional techniques have been proposed.² Routine analysis and novel experiments for small, large, and biomolecules/macromolecular systems are now possible with well-developed simulation packages.³ In addition, sample spinning at the magic angle has now become possible at speeds higher than 50 kHz resulting in very highly ordered and resolved spectra in the solid state.⁴

In this paper we present a general analytic procedure for nuclear spins coupled by strong dipolar interactions and with or without electric quadrupolar interactions. Our objective is to emphasize and expand the derivation of effective Hamiltonians for which analytic solutions are possible for spins coupled to each other as well as to systematize the procedure.⁵ Floquet theory,^{6–9} coupled with van Vleck perturbation theory¹⁰ (also known as the contact transformation method) is used to determine effective Hamiltonians of a spin system subject to sample rotation at high speeds at the magic angle. Their utility is demonstrated by providing simple, yet clear simulations of the spectra of two, three, and four spins coupled through anisotropic interactions and by examining nuclei with quadrupolar interactions. The purpose of the paper is twofold: provide a systematic procedure for coupled spins as the network of spins expands and to demonstrate the utility of analytically derived Hamiltonians in numerical simulations as opposed to the current brute-force procedure of numerical diagonalization of Floquet Hamiltonians. We hope that this will also enable the avid

programmer/simulation developer with the tools necessary to integrate effective Floquet Hamiltonians for analyzing spectra through multiple-pulse experiments.

The procedure we use is the following. The Floquet Hamiltonian is given for a generalized Hamiltonian of N-spins which are coupled by anisotropic dipolar interactions and having non-negligible electric quadrupolar interactions (for $I \geq 1$) in a rotating coordinate system under magic angle spinning conditions, by a standard procedure originally due to Shirley.⁹ The time-independent Floquet Hamiltonian is usually evaluated using an infinite-dimensional basis set which is a direct product of the spin and Fourier space.^{7,8} Although the periodicity of the problem results in eigenvalues that are periodic in nature, the convergence criterion requires diagonalizing matrices of large dimension. A solution to this problem was proposed earlier by one of us in terms of effective Hamiltonians derived from the method of the contact transformation. The contact transformation method is an operator equivalent of the standard Rayleigh–Schrodinger perturbation theory, wherein the perturbation corrections are obtained in terms of operators as opposed to matrix elements in the conventional approach.¹⁰ Employing this approach, effective Floquet Hamiltonians were derived in simple model two-spin systems, both in the Floquet-state space and the Floquet–Liouville space.^{5,9} In this article we extend this approach by presenting a generalized form for effective Floquet Hamiltonians that describes the dynamics of N-interacting spins in magic angle spinning (MAS) experiments. The generalized expression for the effective Hamiltonian finds utility in a wide variety of systems ranging from single spin (both $I=1/2$ and $I > 1/2$ systems) to interacting spin systems. The complexities involved in the standard Floquet approach⁷ are removed using our approach, resulting in a description that principally depends only on the spin dimension of the problem (For example see Ref. 7). Such an approach facilitates the integration of analytic Floquet treatments with numerical

^{a)}Author to whom correspondence should be addressed. Electronic mail: mangal@iitm.ac.in.

simulation programs.³ The validity of effective Hamiltonians derived is demonstrated through simple, yet illustrative simulations.

In the next section, we present the general methodology for deriving effective Hamiltonians for an interacting N-spin system. In Sec. III we present numerical simulations using analytic results of Sec. II for a few model systems.

II. THEORY AND METHODOLOGY

A. Effective Floquet Hamiltonians for an interacting N-spin system

The Hamiltonian under MAS conditions for an interacting N-spin system is represented by

$$\begin{aligned}
 H(t) = & \sum_{\lambda=1}^N \sum_{m=-2}^2 \omega_{\lambda}^{(m)} e^{im\omega_r t} I_{\lambda z} \\
 & + \sum_{\lambda < \mu=1}^N \sum_{\substack{m=-2, \\ m \neq 0}}^2 \omega_{\lambda\mu}^{(m)} e^{im\omega_r t} \left[2I_{\lambda z} I_{\mu z} - \frac{1}{2} (I_{\lambda}^+ I_{\mu}^- + I_{\lambda}^- I_{\mu}^+) \right] \\
 & + \sum_{\lambda=1}^N \sum_{\substack{m=-2, \\ m \neq 0}}^2 \omega_{\lambda Q}^{(m)} e^{im\omega_r t} [3I_{\lambda z}^2 - I_{\lambda}^2], \quad (1)
 \end{aligned}$$

where ω_r is the spinning frequency and $\omega_{\lambda}^{(0)}/\omega_{\lambda}^{(m)}$ represent isotropic/anisotropic interactions of the spins (denoted by the label λ), respectively. Specifically, the isotropic chemical shift associated with a particular spin is represented by $\omega_{\lambda}^{(0)}$, while the anisotropic contributions emerging from the chemical shift [commonly referred to as chemical shift anisotropy (CSA)], dipolar and quadrupolar interactions (only for nuclei with $I \geq 1$) are denoted by $\omega_{\lambda}^{(m)}$, $\omega_{\lambda\mu}^{(m)}$, and $\omega_{\lambda Q}^{(m)}$, respectively. The anisotropic interactions transform as second rank tensors and are commonly defined in the principal axis system. The transformation to the laboratory axis from the principal axis frame is defined by the Wigner rotation matrices [represented by $D_{m_1 m_2}^{(2)}(\Omega)$],

$$\omega_{\lambda}^{(m)} = \sum_{m_1, m_2=-2}^2 D_{m_2 m}^{(2)}(\Omega_{MR}) D_{m_1 m_2}^{(2)}(\Omega_{PM}) R_{\lambda}^{(2) m_1},$$

$$\omega_{\lambda\mu}^{(m)} = \sum_{m_1, m_2=-2}^2 D_{m_2 m}^{(2)}(\Omega'_{MR}) D_{m_1 m_2}^{(2)}(\Omega'_{PM}) R_{\lambda\mu}^{(2) m_1},$$

and

$$\omega_{\lambda Q}^{(m)} = \sum_{m_1, m_2=-2}^2 D_{m_2 m}^{(2)}(\Omega''_{MR}) D_{m_1 m_2}^{(2)}(\Omega''_{PM}) R_{\lambda Q}^{(2) m_1}, \quad (2)$$

with $R_{\lambda}^{(2) m_1}$, $R_{\lambda\mu}^{(2) m_1}$, and $R_{\lambda Q}^{(2) m_1}$ denoting the principal components of the irreducible spatial tensors associated with the chemical shift, dipolar and quadrupolar interactions, respectively, defined in their respective principal axis frames. In the principal axis frame of the chemical shift tensor, $R_{\lambda}^{(2) 0} = \delta_{anis}$ and $R_{\lambda}^{(2) \pm 2} = -(1/\sqrt{6})\delta_{anis}\eta_{\lambda}$ (where δ_{anis} and η represent the chemical shift anisotropy and the asymmetry parameter, respectively) while the dipolar tensor

between the two spins is $R_{\lambda\mu}^{(2) 0} = \sqrt{6}b_{\lambda\mu}$ [where $b_{\lambda\mu} = \mu_0\gamma_{\lambda}\gamma_{\mu}\hbar/4\pi r_{\lambda\mu}^3$ (rad/s) is the dipolar coupling constant] defined in the dipolar principal axis frame. The quadrupolar interactions are defined in the quadrupolar principal axis frame with $R_{\lambda Q}^{(2) 0} = \sqrt{6}\omega_{\lambda Q}$ and $R_{\lambda Q}^{(2) \pm 2} = -\omega_{\lambda Q}\eta_{\lambda Q}$ [where $\omega_{\lambda Q} = e^2q_{\lambda}Q_{\lambda}/4I_{\lambda}(2I_{\lambda}-1)\hbar$ and $\eta_{\lambda Q}$ represent the quadrupolar coupling constant and the asymmetry parameter of quadrupolar nuclei, respectively], being the only nonzero components for an axially asymmetric tensor.

Employing the Floquet theorem, the time-dependent Hamiltonian [as given in Eq. (1)] is transformed into a time-independent Hamiltonian via Fourier series expansion. The resulting time-independent Hamiltonian (commonly referred to as Floquet Hamiltonian) is described in an infinite-dimensional basis set constructed from a direct product between the standard spin operator basis (described in a finite-dimensional vector space) and the Fourier operator basis (described in an infinite-dimensional vector space known as the Floquet space). In this article we employ an operator basis constructed from the direct product between the fictitious spin-1/2 operators (single transition operators) and the Fourier operators.⁸

Employing this operator basis, the time-independent Floquet Hamiltonian, H^F , is represented by

$$\begin{aligned}
 H^F = & \sum_{p=1}^{2^N} \omega_r I^{p,p} + \sum_{p=1}^{2^N} z_0^{p,p} Z_0^{p,p} + \sum_{p=1}^{2^N} \sum_{\substack{m=-2 \\ \neq 0}}^2 z_m^{p,p} Z_m^{p,p} \\
 & + \sum_{\lambda < \mu=1}^N \sum_{p,q} \sum_{\substack{m=-2 \\ \neq 0}}^2 X_{\lambda\mu,m}^{p,q} X_m^{p,q}, \quad (3)
 \end{aligned}$$

where 2^N is the total number of basis states (denoted by p) employed for describing an N-spin system. The first term may be identified with the number operator in the Floquet basis, while the time-dependent and time-independent terms illustrated in Eq. (1) are associated with the operators $X_m^{p,q}$ and $Z_m^{p,p}$ with $m \neq 0$ and $m=0$, respectively. The $Z_m^{p,p}$ operators connect Floquet states $|p, n\rangle$ and $|p, m+n\rangle$ that differ only in the Fourier dimension and are associated with the longitudinal single spin $I_{\lambda z}$ (chemical shift anisotropy) and bilinear operators $I_{\lambda z} I_{\mu z}$ and $3I_{\lambda z}^2 - I_{\lambda}^2$ associated with the dipolar and quadrupolar interactions, respectively, as depicted in Eq. (1). The last term comprised of the $X_m^{p,q}$ operators connects states $|p, n\rangle$ and $|q, m+n\rangle$ that differ both in the spin and Fourier dimension and is commonly associated with the flip-flop operators in the dipolar interactions as described in Eq. (1) and Table I.

The time-independent coefficients associated with a particular state “ p ” are represented by the $z_0^{p,p}$ coefficients in terms of the isotropic chemical shifts $\omega_{\lambda}^{(0)}$ of the spins, i.e., $z_0^{p,p} = \sum_{\lambda=1}^N 2m_p^{(\lambda)} \omega_{\lambda}^{(0)}$. The anisotropic interactions corresponding to the chemical shift, $\omega_{\lambda}^{(m)}$ (CSA) and dipolar interactions ($\omega_{\lambda\mu}^{(m)}$) are represented by the coefficients

TABLE I. States connected by the flip-flop operators $X_m^{p,q}$ for spins λ and μ . The indices p and q represent the spin states and depend on the spin topology. In the case of a two-spin system, $1 \equiv |\alpha\alpha\rangle$, $2 \equiv |\alpha\beta\rangle$, $3 \equiv |\beta\alpha\rangle$, and $4 \equiv |\beta\beta\rangle$, while $1 \equiv |\alpha, \alpha, \alpha\rangle$, $2 \equiv |\alpha, \alpha, \beta\rangle, \dots, 8 \equiv |\beta, \beta, \beta\rangle$ and $1 \equiv |\alpha, \alpha, \alpha, \alpha\rangle$, $2 \equiv |\alpha, \alpha, \alpha, \beta\rangle, \dots, 16 \equiv |\beta, \beta, \beta, \beta\rangle$ in the cases of three and four spins, respectively.

Two spins				Three spins				Four spins							
$\lambda=1$	$\mu=2$	p	2	$\lambda=1$	$\mu=2$	p	3	4	$\lambda=1$	$\mu=2$	p	5	6	7	8
		q	3			q	5	6			q	9	10	11	12
				$\lambda=1$	$\mu=3$	p	2	4	$\lambda=1$	$\mu=3$	p	3	4	7	8
						q	5	7			q	9	10	13	14
				$\lambda=2$	$\mu=3$	p	2	6	$\lambda=1$	$\mu=4$	p	2	4	6	8
						q	3	7			q	9	11	13	15
									$\lambda=2$	$\mu=3$	p	3	4	11	12
											q	5	6	13	14
									$\lambda=2$	$\mu=4$	p	2	4	10	12
											q	5	7	13	15
									$\lambda=3$	$\mu=4$	p	2	6	10	14
											q	3	7	11	15

$$z_m^{p,p} = \sum_{\lambda=1}^N 2m_p^{(\lambda)} \omega_{\lambda}^{(m)} + \sum_{\lambda < \mu=1}^N 4m_p^{(\lambda)} m_p^{(\mu)} \omega_{\lambda\mu}^{(m)},$$

$$x_{\lambda\mu,m}^{p,q} = -\omega_{\lambda\mu}^{(m)} (\text{for } I=1/2),$$

while, for quadrupolar systems ($I \geq 1$), they are given by

$$z_m^{p,p} = \sum_{\lambda=1}^N 2m_p^{(\lambda)} \omega_{\lambda}^{(m)} + \sum_{\lambda < \mu=1}^N 4m_p^{(\lambda)} m_p^{(\mu)} \omega_{\lambda\mu}^{(m)} + 2\omega_{\lambda Q}^{(m)} \\ \times [3(m_p^{(\lambda)})^2 - I_{\lambda}(I_{\lambda} + 1)]$$

(where $m_p^{(\lambda)}$ denotes the magnetic quantum number associated with spin “ λ ” corresponding to the state p). For the specific case of $I=1$, $x_{\lambda\mu,m}^{p,q} = -2\omega_{\lambda\mu}^{(m)}$.

B. Application of the contact transformation method

To eliminate the complexity associated with the infinite dimensionality of the problem, the concept of effective Floquet Hamiltonians derived from the contact transformation method was proposed in earlier publications.^{5,11} We demonstrate the utility of this approach in deriving effective Hamiltonians for an interacting N-spin system.

In the contact transformation method, the Floquet Hamiltonian [Eq. (3)] is split into a zero-order Hamiltonian, H_0^F , and a perturbing Hamiltonian, H_1^F . The zero-order Hamiltonian is chosen to contain operators that are diagonal in the Fourier dimension ($m=0$) while the perturbing Hamiltonian comprises operators that are off-diagonal in the Fourier dimension ($m \neq 0$), namely,

$$H_0^F = \sum_{p=1}^{2^N} \omega_p I^{p,p} + \sum_{p=1}^{2^N} z_0^{p,p} Z_0^{p,p}, \quad (4a)$$

$$H_1^F = \sum_{p=1}^{2^N} \sum_{m=-2}^2 z_m^{p,p} Z_m^{p,p} + \sum_{\lambda < \mu=1}^N \sum_{p,q} \sum_{m=-2}^2 x_{\lambda\mu,m}^{p,q} X_m^{p,q}, \quad (4b)$$

where the choice of p and q depends on the choice of λ and μ as described in Table I.

Employing a single or a series of unitary transformations, the original Hamiltonian, H^F , is transformed into an effective Hamiltonian, H_{eff}^F , i.e.,

$$H_{\text{eff}}^F = \cdots U_n \cdots U_2 U_1 H^F U_1^{-1} U_2^{-1} \cdots U_n^{-1} \cdots.$$

We derive an effective Hamiltonian by employing a single unitary transformation

$$H_{\text{eff}}^F = U_1 H^F U_1^{-1} = e^{i\lambda S_1} H^F e^{-i\lambda S_1} \\ = H_0^{(1)F} + \lambda H_1^{(1)F} + \lambda^2 H_2^{(1)F} \cdots, \quad (5a)$$

$$H_0^{(1)F} = H_0^F, \quad (5b)$$

$$H_1^{(1)F} = H_1^F + i[S_1, H_0^F], \quad (5c)$$

$$H_2^{(1)F} = H_2^F + i[S_1, H_1^F] - \frac{1}{2}[S_1, [S_1, H_0^F]], \quad (5d)$$

where the terms $H_0^{(1)F}$, $H_1^{(1)F}$, and $H_2^{(1)F}$ represent the zero-order, first-order, and second-order corrections after the first transformation, respectively. In the present description of the system, H_2^F is zero as all the perturbing terms are included in H_1^F . The transformation function S_1 [illustrated in Eq. (5c)] is properly chosen to compensate the Off diagonality in H_1^F and in general can be expressed as a linear combination of a complete set of operators employed in describing the perturbing Hamiltonian,

$$S_1 = i \left[\sum_{p=1}^{2^N} \sum_{m=-2}^2 A_m^{(p)} Z_m^{p,p} \right] \\ - i \left[\sum_{\lambda < \mu=1}^N \sum_{p,q} \sum_{m=-2}^2 \{ C_{\lambda\mu,m}^{p,q} X_m^{p,q} + i B_{\lambda\mu,m}^{p,q} Y_m^{p,q} \} \right]. \quad (6)$$

The coefficients in the transformation function S_1 are obtained by solving Eq. (5c) and can be generalized for an N-spin system by the following equation which represents a system of coupled linear equations in the coefficients given in Eq. (6),

$$H_1^F + i[S_1, H_0^F] = 0. \quad (7)$$

General expressions for the constants associated with the S_1 functions are obtained as

$$A_m^{(p)} = \frac{z_m^{p,p}}{m\omega_r}, \quad B_{\lambda\mu,m}^{p,q} = \frac{C_{\lambda\mu,m}^{p,q}(z_0^{p,p} - z_0^{q,q})}{2m\omega_r}, \quad (8)$$

$$C_{\lambda\mu,m}^{p,q} = \frac{-4x_{\lambda\mu,m}^{p,q}m\omega_r}{4m^2\omega_r^2 - (z_0^{p,p} - z_0^{q,q})^2}.$$

Subsequently, the diagonal corrections to second-order are obtained by evaluating the right hand side of Eq. (5d) to give

$$H_{2,d}^{(1)F} = -\frac{1}{2} \left[\sum_{m=-2}^{+2} \left\{ \sum_{\lambda < \mu=1}^N \sum_{p,q} \left\{ x_{\lambda\mu,-m}^{p,q} B_{\lambda\mu,m}^{p,q} (Z_0^{q,q} - Z_0^{p,p}) \right. \right. \right. \\ \left. \left. \left. + x_{\lambda\mu,-m}^{p,q} (A_m^{(p)} - A_m^{(q)}) \frac{i}{2} Y_0^{p,q} \right\} \right. \right. \\ \left. \left. + \sum_{\lambda_1 < \mu < \lambda_2=1}^N \sum_{p,q,r} \left\{ (x_{\lambda_1\mu,-m}^{p,q} B_{\lambda_2\mu,m}^{q,r} \right. \right. \right. \\ \left. \left. \left. - x_{\lambda_2\mu,-m}^{q,r} B_{\lambda_1\mu,m}^{p,q} \frac{1}{2} X_0^{p,r} + (x_{\lambda_1\mu,-m}^{p,q} C_{\lambda_2\mu,m}^{q,r} \right. \right. \right. \\ \left. \left. \left. - x_{\lambda_2\mu,-m}^{q,r} C_{\lambda_1\mu,m}^{p,q} \frac{i}{2} Y_0^{p,r} \right\} \right] \right]. \quad (9)$$

In the second-order corrections [Eq. (9)], the first set of terms summed over p and q on the right hand side contains Z operators which result from cross-terms between the dipolar interactions associated with different “ m ” values, while the X and Y operators result from cross-terms between the CSA and the dipolar interactions associated with a particular spin pair. The second set of terms summed over p , q , and r is obtained only in systems comprising of more than two spins resulting from dipolar cross-terms between spin pairs (λ_1, μ) and (μ, λ_2) .

The transformed effective Floquet Hamiltonian (to second-order) is given by

$$H_{\text{eff}}^F = \sum_{p=1}^{2^N} \omega_r I^{p,p} + \sum_{p=1}^{2^N} z_0^{p,p} Z_0^{p,p} + H_{2,d}^{(1)F}. \quad (10)$$

In the next section we demonstrate the utility of the above, generalized effective Hamiltonians in describing the spin dynamics in systems ranging from single spin ($I=1/2$) to four-spin dipolar-coupled and quadrupolar systems. The advantages associated with this approach are substantiated with simulations based on the analytic theory.

III. ANALYTIC SIMULATIONS AND DISCUSSION

A. Effective Hamiltonians for noninteracting spin systems ($I=1/2$)

1. Single spin

Following the description in the previous section, the time-dependent Hamiltonian under MAS conditions for a single spin-1/2 is given by

$$H(t) = \sum_{m=-2}^2 \omega^{(m)} e^{im\omega_r t} I_z. \quad (11)$$

After the Floquet transformation the time-independent Hamiltonian, H^F is given by

$$H^F = \sum_{p=1}^2 \omega_r I^{p,p} + \sum_{p=1}^2 z_0^{p,p} Z_0^{p,p} + \sum_{p=1}^2 \sum_{\substack{m=-2 \\ m \neq 0}}^2 z_m^{p,p} Z_m^{p,p}, \quad (12)$$

where the superscripts $p=1$ and $p=2$ denote the two-spin states $|1/2\rangle$ and $|-1/2\rangle$, respectively. The constants associated with various operators in the Hamiltonian in Eq. (12) are given by

$$z_0^{1,1} = \omega^{(0)}, \quad z_0^{2,2} = -\omega^{(0)},$$

$$z_m^{1,1} = \omega^{(m)}, \quad z_m^{2,2} = -\omega^{(m)}.$$

The Floquet Hamiltonian [Eq. (11)] is split into a zero-order Hamiltonian H_0^F and a perturbing Hamiltonian H_1^F , given by

$$H_0^F = \sum_{p=1}^2 \omega_r I^{p,p} + \sum_{p=1}^2 z_0^{p,p} Z_0^{p,p} \quad \text{and} \quad (13a)$$

$$H_1^F = \sum_{p=1}^2 \sum_{\substack{m=-2 \\ m \neq 0}}^2 z_m^{p,p} Z_m^{p,p}. \quad (13b)$$

The transformation function S_1 is determined as described earlier and is represented by

$$S_1 = i \left[\sum_{p=1}^2 \sum_{\substack{m=-2 \\ m \neq 0}}^2 \frac{z_m^{p,p}}{m\omega_r} Z_m^{p,p} \right]. \quad (14)$$

Since the transformation function contains only the $Z_m^{p,p}$ operators, the second-order corrections $H_2^{(1)F}$, tend to zero, i.e.,

$$H_2^{(1)F} = \frac{i}{2} [S_1, H_1^F], \quad (15a)$$

$$H_{2,d}^{(1)F} = -\frac{1}{2} \left[\sum_{p=1}^2 \sum_{\substack{m=-2 \\ m \neq 0}}^2 A_m^{(p)} Z_m^{p,p}, \sum_{p=1}^2 \sum_{\substack{m=-2 \\ m \neq 0}}^2 z_m^{p,p} Z_m^{p,p} \right] = 0. \quad (15b)$$

Hence, the effective Hamiltonian for a single spin or a system of noninteracting spins is comprised only of the isotropic chemical shift of the individual spins

$$H_{\text{eff}}^F = H_0^F. \quad (16)$$

The calculation of sideband intensities, however, requires the exponential terms operating on the detection operator and the corresponding operators do not commute with each other. Therefore, perturbation theory approach is used here to determine the S_1 function required for the calculation of the sideband intensities.

2. Simulation of MAS spectra

The time-domain signal is calculated by evaluating the expectation value of the detection operator, $(I_-)_0^{p,q}$,

$$\begin{aligned} \langle (I_-)_0^{p,q} \rangle &= \text{Tr}[\rho^F(t)(I_-)_0^{p,q}] \\ &= \sum_{m=-\infty}^{\infty} \sum_{p=1}^2 \langle p, m | [\rho^F(t)(I_-)_0^{p,q}] | p, m \rangle, \end{aligned} \quad (17a)$$

where $\rho^F(t) = e^{-iH^F t} \rho^F(0) e^{iH^F t}$, such that $\rho^F(0) = (I_+)_0^{p,q} = (X_0^{1,2} + iY_0^{1,2})$ represents the initial density matrix immediately after a radiofrequency pulse and $\{|p, m\rangle\}$ are the Floquet states, constructed from the direct product of the spin basis ($p=1$ and 2) with the Fourier basis states, $m=-\infty, \dots, -1, 0, 1, \dots, \infty$. Expressing the density matrix and the detection operator in the transformed basis defined by S_1 , Eq. (17a) is expanded as follows:

$$\begin{aligned} \langle (I_-)_0^{p,q} \rangle &= \sum_{m=-\infty}^{\infty} \sum_{p=1}^2 \langle p, m | U^{-1} U e^{-iH^F t} U^{-1} U \rho^F(0) U^{-1} U e^{iH^F t} U^{-1} U | q, n \rangle \langle q, n | U^{-1} U (I_-)_0^{p,q} U^{-1} U | p, m \rangle \\ &= \sum_{m,n=-\infty}^{\infty} \sum_{i,j=1}^2 \langle \psi_i^{(m)} | e^{-iH_{\text{eff}}^F t} \rho^F(0) e^{iH_{\text{eff}}^F t} | \psi_j^{(n)} \rangle \langle \psi_j^{(n)} | (I_-)_0^{p,q} | \psi_i^{(m)} \rangle, \end{aligned} \quad (17b)$$

where $U = e^{iS_1}$ is the unitary transformation operator, $\rho^F(0) = U(I_+)_0^{p,q} U^{-1}$ is the effective time-dependent density operator, $(I_+)_0^{p,q} = U(I_+)_0^{p,q} U^{-1}$ and $|\psi_i^{(m)}\rangle$ are the eigenfunctions of the effective Floquet Hamiltonian H_{eff}^F . In the expansion of both $\rho^F(0)$ and $(I_+)_0^{p,q}$, the higher-order (second-order in our case) terms have been neglected, i.e.,

$$\rho^F(0) = e^{iS_1} (I_+)_0^{p,q} e^{-iS_1} \approx (I_+)_0^{p,q} + \frac{z_m^{p,q}}{m\omega_r} (I_+)_m^{p,q}. \quad (17c)$$

To eliminate the redundancy in Eq. (17b), one of the Fourier summation coefficients n is set to zero. Furthermore, owing to the periodicity of the problem, the eigenvalues (depicted by $\lambda_i^{(0)}$) in the Floquet space can be calculated by evaluating the supereigenvalues corresponding to the diagonal block, $m=0$. Subsequently, the time-domain signal is calculated by re-expressing Eq. (17b) in a convenient form depicting the center-band (matrix elements of operators with zero as subscript) and the side-band contributions to the MAS spectrum as

$$\begin{aligned} \langle (I_-)_0^{p,q}(t) \rangle &= \sum_{i,j=1}^2 \langle \psi_i^{(m)} | (I_+)_0^{p,q} | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | (I_-)_0^{p,q} | \psi_i^{(m)} \rangle e^{i(\lambda_i^{(0)} - \lambda_j^{(0)})t} \\ &+ \sum_{m \neq 0} \sum_{i,j=1}^2 \left(\frac{z_m^{p,q} z_m^{p,q*}}{m^2 \omega_r^2} \right) \langle \psi_i^{(m)} | (I_+)_m^{p,q} | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | \\ &\times (I_-)_m^{p,q} | \psi_i^{(m)} \rangle e^{i((\lambda_i^{(0)} - \lambda_j^{(0)}) + m\omega_r)t}. \end{aligned} \quad (17d)$$

To simulate the MAS powder spectrum, the above equation is evaluated for different crystallite orientations, which on Fourier transformation lead to the MAS spectrum in the frequency-domain in Fig. 1. In the simulations presented, sidebands corresponding to $m = \pm 1$ and ± 2 are depicted.

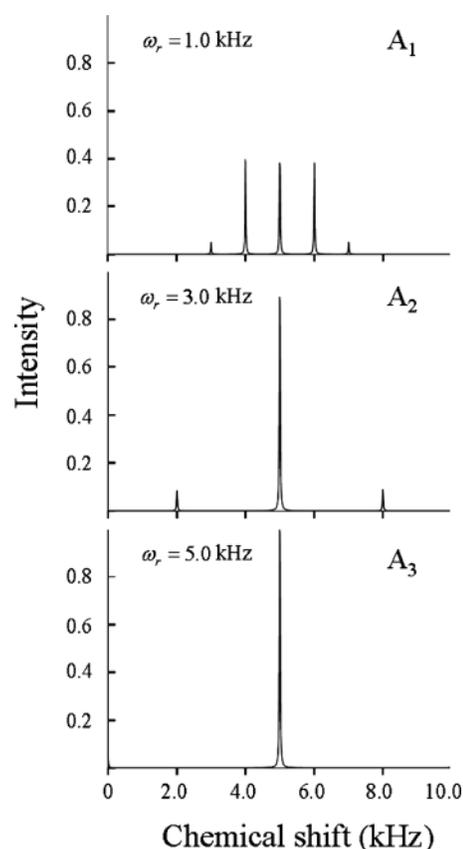


FIG. 1. Simulated ^{13}C MAS spectra for a single spin-1/2 system at 100 MHz (^{13}C) frequency. The following CSA parameters were employed in the simulations: σ_{xx} , σ_{yy} , and σ_{zz} equal to 35, 50, and 65 ppm, respectively; CSA orientations α_{PM} , β_{PM} , and γ_{PM} equal to 70° , 60° , and 122° , respectively. Gaussian line broadening of 70 Hz was employed in the simulations.

Higher-order sidebands can be calculated by evaluating the higher-order terms in the expansion of $\rho'^F(0)$ and $(I_{\pm})_0^{p,q}$ in Eq. (17c). Following the standard procedure, the intensities are normalized with respect to the center-band by including the contributions emerging from the sidebands, i.e.,

$$\langle I_{-}^{pq}(t) \rangle = \sum_{m=-2}^2 \frac{C_m^2}{C_0^2 + C_{-1}^2 + C_{-2}^2 + C_1^2 + C_2^2}, \quad (17e)$$

where C_0^2 represents the intensity of the center-band and C_i^2 the corresponding intensity of the sidebands. In the slow-spinning regime higher-order contributions resulting in higher sidebands ($m > 2$) need to be evaluated in the intensity expression. As the spinning frequency of the sample increases, contributions from the CSA decrease, resulting in the decrease in the intensity of the sidebands and leading to improved sensitivity and resolution. This aspect of the procedure is illustrated in Fig. 1 which depicts simulations of MAS spectrum at three different spinning frequencies.

B. Effective Hamiltonians for interacting spin systems

1. Two spins

The time-dependent MAS Hamiltonian for a homonuclear dipolar-coupled spin pair is represented by

$$H(t) = \sum_{\lambda=1}^2 \sum_{m=-2}^2 \omega_{\lambda}^{(m)} e^{im\omega_r t} I_{\lambda z} + \sum_{m=-2, m \neq 0}^2 \omega_{12}^{(m)} e^{im\omega_r t} \times [2I_{1z}I_{2z} - \frac{1}{2}(I_1^+I_2^- + I_1^-I_2^+)]. \quad (18)$$

Employing the procedure described in the previous section, the Floquet Hamiltonian for a dipolar-coupled system is split into a zero-order Hamiltonian, H_0^F , and a perturbing Hamiltonian, H_1^F (the two groups of terms on the right side, respectively),

$$H^F = \left\{ \sum_{p=1}^4 \omega_r I^{p,p} + \sum_{p=1}^4 z_0^{p,p} Z_0^{p,p} \right\} + \left\{ \sum_{p=1}^4 \sum_{\substack{m=-2 \\ \neq 0}}^2 z_m^{p,p} Z_m^{p,p} + \sum_{\substack{m=-2 \\ \neq 0}}^2 x_{12,m}^{2,3} X_m^{2,3} \right\}. \quad (19)$$

The transformation function S_1 is expressed in terms of a complete basis set of operators as

$$S_1 = i \left[\sum_{p=1}^4 \sum_{\substack{m=-2 \\ \neq 0}}^2 A_m^{(p)} Z_m^{p,p} \right] - i \left[\sum_{\substack{m=-2 \\ \neq 0}}^2 \{ (C_{12,m}^{2,3} X_m^{2,3} + i B_{12,m}^{2,3} Y_m^{2,3}) \} \right]. \quad (20a)$$

Employing Eq. (8), the coefficients in the transformation function S_1 for a dipolar-coupled spin pair are obtained as

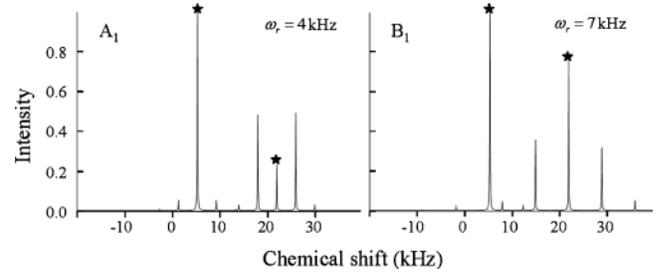


FIG. 2. A_1 and B_1 represent simulated ^{13}C MAS spectra for a homonuclear dipolar-coupled two spin-1/2 system obtained at two different spinning frequencies. The following CSA parameters were employed: CSA orientations $\alpha_{PM}^{(1)}$, $\beta_{PM}^{(1)}$, $\gamma_{PM}^{(1)}$, $\alpha_{PM}^{(2)}$, $\beta_{PM}^{(2)}$, and $\gamma_{PM}^{(2)}$ equal to 160° , 33° , $90^\circ/119^\circ$, 94° , and -13° , asymmetry parameters η_1/η_2 equal to 1.0/0.91, isotropic chemical shifts $\omega_1^{(0)}/\omega_2^{(0)}$ (denoted by asterisk) equal to 21.87 kHz/5.25 kHz and chemical shift anisotropies δ_1/δ_2 equal to 8.54 kHz/1.41 kHz. The dipolar coupling strength was set to 457 Hz ($r_{12}=2.55 \text{ \AA}$).

$$A_m^{(p)} = \frac{z_m^{p,p}}{m\omega_r}, \quad B_{12,m}^{2,3} = \frac{-C_{12,m}^{2,3}(z_0^{3,3} - z_0^{2,2})}{2m\omega_r}, \quad (20b)$$

$$C_{12,m}^{2,3} = \frac{-4x_{12,m}^{2,3}m\omega_r}{4m^2\omega_r^2 - (z_0^{3,3} - z_0^{2,2})^2}.$$

In a similar vein, the second-order corrections to the zero-order Hamiltonian can be written down by employing Eq. (9) as

$$H_{2,d}^{(1)F} = -\frac{1}{2} \left[\sum_{\substack{m=-2 \\ m \neq 0}}^2 \left\{ -x_{12,-m}^{2,3} B_{12,m}^{2,3} (Z_0^{2,2} - Z_0^{3,3}) + (z_{-m}^{2,2} - z_{-m}^{3,3}) \frac{B_{12,m}^{2,3}}{2} X_0^{2,3} + \{ (z_{-m}^{2,2} - z_{-m}^{3,3}) C_{12,m}^{2,3} + x_{12,-m}^{2,3} (A_m^{(2)} - A_m^{(3)}) \} \frac{i}{2} Y_0^{2,3} \right\} \right]. \quad (21)$$

In contrast with the single spin $I=1/2$ system, the second-order corrections comprise the operators $X_0^{2,3}$, $Y_0^{2,3}$, and $Z_0^{2,3}$. Following the standard procedure described in the previous section, the frequency-domain spectrum for a dipolar-coupled spin pair is calculated and is depicted in Fig. 2. The reduced central transition intensity in the case of $\omega_r = 4 \text{ kHz}$ is most certainly due to a higher CSA value and a lower rotational frequency for that particular nucleus. As ω_r increases perturbation corrections are more meaningful and the central transition intensity increases obviously.

2. Three spins

The Hamiltonian for a dipolar-coupled three-spin ($I=1/2$) system under MAS is represented by

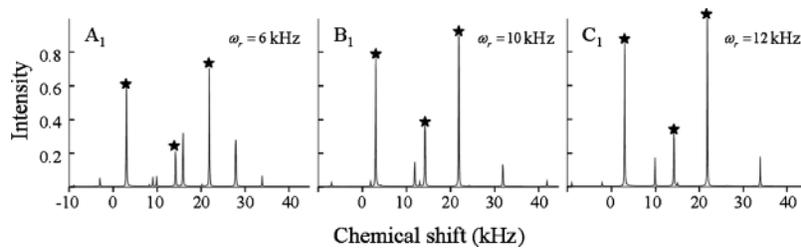


FIG. 3. A_1 , B_1 , and C_1 represent the simulated ^{13}C MAS spectra for a three-spin dipolar-coupled system at different spinning frequencies. The following chemical shift parameters were employed: $\alpha_{PM}^{(1)}=160^\circ$, $\beta_{PM}^{(1)}=33^\circ$, $\gamma_{PM}^{(1)}=90^\circ$, $\eta_1=1.0$, $\delta_1=8.54$ kHz, $\omega_1^{(0)}=21.87$ kHz, $\alpha_{PM}^{(2)}=119^\circ$, $\beta_{PM}^{(2)}=94^\circ$, $\gamma_{PM}^{(2)}=-13^\circ$, $\eta_2=0.91$, $\delta_2=1.41$ kHz, $\omega_2^{(0)}=14.2$ kHz and $\alpha_{PM}^{(3)}=-49^\circ$, $\beta_{PM}^{(3)}=48^\circ$, $\gamma_{PM}^{(3)}=-170^\circ$, $\eta_3=0.92$, $\delta_3=3.0$ kHz, $\omega_3^{(0)}=3.0$ kHz. The dipolar parameters employed were $r_{12}=2.55$ Å, $r_{13}=3.72$ Å, and $r_{23}=5.9$ Å (^{13}C - ^{13}C dipolar coupling strength at 1 Å internuclear distance is equal to 7.5859 kHz). The asterisks denote the position of the center-band associated with the isotropic chemical shifts of the three spins.

$$H(t) = \sum_{\lambda=1}^3 \sum_{m=-2}^2 \omega_{\lambda}^{(m)} e^{im\omega_r t} I_{\lambda z} + \sum_{\lambda < \mu = 1}^3 \sum_{\substack{m=-2, \\ m \neq 0}}^2 \omega_{\lambda\mu}^{(m)} e^{im\omega_r t} \left[2I_{\lambda z} I_{\mu z} - \frac{1}{2}(I_{\lambda}^+ I_{\mu} + I_{\lambda} I_{\mu}^+) \right]. \quad (22)$$

The Floquet Hamiltonian for a three-spin dipolar-coupled system is expressed as

$$H^F = \left\{ \sum_{p=1}^8 \omega_r I^{p,p} + \sum_{p=1}^8 z_0^{p,p} Z_0^{p,p} \right\} + \left\{ \sum_{p=1}^8 \sum_{\substack{m=-2 \\ \neq 0}}^2 z_m^{p,p} Z_m^{p,p} + \sum_{m=-2}^2 [x_{23,m}^{2,3} X_m^{2,3} + x_{23,m}^{6,7} X_m^{6,7} + x_{13,m}^{2,5} X_m^{2,5} + x_{13,m}^{4,7} X_m^{4,7} + x_{12,m}^{3,5} X_m^{3,5} + x_{12,m}^{4,6} X_m^{4,6}] \right\}. \quad (23)$$

The transformation function S_1 for a three-spin system is represented by

$$S_1 = i \left[\sum_{p=1}^8 \sum_{\substack{m=-2 \\ \neq 0}}^2 A_m^{(p)} Z_m^{p,p} \right] - i \left[\sum_{m=-2}^2 \{ (C_{23,m}^{2,3} X_m^{2,3} + iB_{23,m}^{2,3} Y_m^{2,3}) + (C_{23,m}^{6,7} X_m^{6,7} + iB_{23,m}^{6,7} Y_m^{6,7}) + (C_{13,m}^{2,5} X_m^{2,5} + iB_{13,m}^{2,5} Y_m^{2,5}) + (C_{13,m}^{4,7} X_m^{4,7} + iB_{13,m}^{4,7} Y_m^{4,7}) + (C_{12,m}^{3,5} X_m^{3,5} + iB_{12,m}^{3,5} Y_m^{3,5}) + (C_{12,m}^{4,6} X_m^{4,6} + iB_{12,m}^{4,6} Y_m^{4,6}) \} \right], \quad (24)$$

with the coefficients having the same functional form as that described in Eq. (8).

The diagonal corrections (in Fourier label) obtained to second-order are given by

$$H_{2,d}^{(1)F} = -\frac{1}{2} \left[\sum_{m=-2}^{+2} \left\{ \sum_{\substack{\lambda < \mu = 1 \\ \neq 0}}^3 \sum_{p,q} \left\{ x_{\lambda\mu,-m}^{p,q} B_{\lambda\mu,m}^{p,q} (Z_0^{q,q} - Z_0^{p,p}) + (z_{-m}^{p,p} - z_{-m}^{q,q}) \frac{B_{\lambda\mu,m}^{p,q}}{2} X_0^{p,q} + \{ (z_{-m}^{p,p} - z_{-m}^{q,q}) C_{\lambda\mu,m}^{p,q} + x_{\lambda\mu,-m}^{p,q} (A_m^{(p)} - A_m^{(q)}) \} \frac{i}{2} Y_0^{p,q} \right\} \right\} + \sum_{\lambda_1 < \mu < \lambda_2 = 1}^3 \sum_{p,q,r} \left\{ (x_{\lambda_1\mu,-m}^{p,q} B_{\lambda_2\mu,m}^{q,r} - x_{\lambda_2\mu,-m}^{q,r} B_{\lambda_1\mu,m}^{p,q}) \times \frac{1}{2} X_0^{p,r} + (x_{\lambda_1\mu,-m}^{p,q} C_{\lambda_2\mu,m}^{q,r} - x_{\lambda_2\mu,-m}^{q,r} C_{\lambda_1\mu,m}^{p,q}) \frac{i}{2} Y_0^{p,r} \right\} \right]. \quad (25)$$

In contrast with the two-spin system, the second-order corrections in the three-spin system comprise both sets of terms, one set which is summed over p and q and the other set which is summed over p , q , and r , for a dipolar coupled N-spins of $I=1/2$. Employing the generalized effective Hamiltonians, simulations have been carried out for a three- and a four-spin system and the results are depicted in Figs. 3 and 4, respectively. In a similar manner one can obtain effective Floquet Hamiltonians for many spins coupled by dipolar interactions from the generalized expression given in the previous section [Eq. (9)].

C. Effective Hamiltonians in dipolar recoupling experiments

In dipolar recoupling experiments, a part of the dipolar interaction represented in Eq. (1) is reintroduced by compensating the spatial averaging rendered by MAS. The theoretical description of such experiments has been described in both the average Hamiltonian¹² and Floquet framework^{7,8} and will not be dealt with in this article. For the purpose of demonstration, we derive the effective Floquet Hamiltonian describing the (rotational resonance) R^2 exchange dynamics from the generalized effective Floquet Hamiltonians presented in the previous section. Following standard description, the Floquet Hamiltonian for a homonuclear dipolar coupled system under R^2 condition is represented by

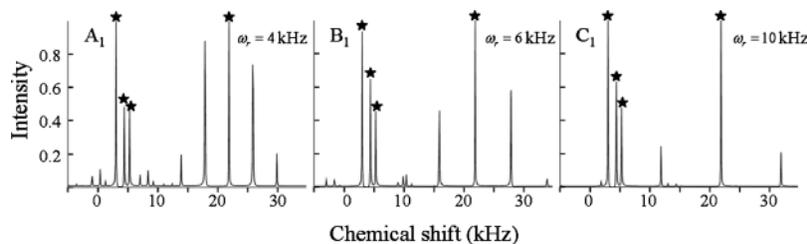


FIG. 4. A₁, B₁, and C₁ represent the simulated ¹³C MAS spectra for a four-spin dipolar-coupled system at different spinning frequencies. The following chemical shift parameters were employed: $\alpha_{PM}^{(1)}=160^\circ$, $\beta_{PM}^{(1)}=33^\circ$, $\gamma_{PM}^{(1)}=90^\circ$, $\eta_1=1.0$, $\delta_1=8.54$ kHz, $\omega_1^{(0)}=21.87$ kHz, $\alpha_{PM}^{(2)}=119^\circ$, $\beta_{PM}^{(2)}=94^\circ$, $\gamma_{PM}^{(2)}=-13^\circ$, $\eta_2=0.91$, $\delta_2=1.41$ kHz, $\omega_2^{(0)}=5.25$ kHz, $\alpha_{PM}^{(3)}=-49^\circ$, $\beta_{PM}^{(3)}=48^\circ$, $\gamma_{PM}^{(3)}=-170^\circ$, $\eta_3=0.92$, $\delta_3=3.0$ kHz, $\omega_3^{(0)}=3.0$ kHz and $\alpha_{PM}^{(4)}=57^\circ$, $\beta_{PM}^{(4)}=147^\circ$, $\gamma_{PM}^{(4)}=120^\circ$, $\eta_4=0.0$, $\delta_4=2.5$ kHz, $\omega_4^{(0)}=4.37$ kHz. The dipolar parameters employed were $r_{12}=2.55$ Å, $r_{13}=3.72$ Å, $r_{23}=5.9$ Å, $r_{14}=5.9$ Å, $r_{24}=7.0$ Å, and $r_{34}=2.55$ Å (¹³C–¹³C dipolar coupling strength at 1 Å internuclear distance is equal to 7.5859 kHz). The asterisks represent the position of the center-band associated with the isotropic chemical shifts of the four spins.

$$H^F = \sum_{p=1}^4 \omega_p I^{p,p} + \sum_{p=1}^4 z_0^{p,p} Z_0^{p,p} + x_{12,0}^{2,3} X_0^{2,3} + iy_{12,0}^{2,3} Y_0^{2,3} + \sum_{p=1}^4 \sum_{\substack{m=-2, \\ m \neq 0}}^2 z_m^{p,p} Z_m^{p,p} + \sum_{\substack{m=-4, \\ m \neq 0}}^4 [x_{12,m}^{2,3} X_m^{2,3} + iy_{12,m}^{2,3} Y_m^{2,3}]. \quad (26)$$

In contrast with the Floquet Hamiltonian for a dipolar-coupled spin pair represented in Eq. (19), the Floquet Hamiltonian for a recoupling experiment consists of $X_0^{2,3}$ and $Y_0^{2,3}$ operators.¹² This form is common to both selective and broadband recoupling schemes in solid state NMR and the description presented below is valid for N-spin systems.

To reduce the complexity in the description involving many spins, the time-independent terms associated with the dipolar interactions (represented by $X_0^{2,3}$ and $Y_0^{2,3}$ operators) are separated from the zero-order Hamiltonian as

$$H^F = H_0^F + H_1^F = H_0^F + H_{1,\text{dia}}^F + H_{1,\text{off-dia}}^F,$$

where

$$H_0^F = \sum_{p=1}^4 \omega_p I^{p,p} + \sum_{p=1}^4 z_0^{p,p} Z_0^{p,p},$$

$$H_{1,\text{dia}}^F = x_{12,0}^{2,3} X_0^{2,3} + iy_{12,0}^{2,3} Y_0^{2,3} \quad \text{and} \quad (27)$$

$$H_{1,\text{off-dia}}^F = \sum_{p=1}^4 \sum_{\substack{m=-2, \\ m \neq 0}}^2 z_m^{p,p} Z_m^{p,p} + \sum_{\substack{m=-4, \\ m \neq 0}}^4 [x_{12,m}^{2,3} X_m^{2,3} + iy_{12,m}^{2,3} Y_m^{2,3}].$$

The transformation function S_1 is chosen to compensate the off-diagonality present in H_1^F (i.e., $H_{1,\text{off-dia}}^F$), by solving Eq. (28),

$$H_1^{(1)F} = H_{1,\text{dia}}^F + H_{1,\text{off-dia}}^F + i[S_1, H_0^F] = H_{1,\text{dia}}^F. \quad (28)$$

The second-order corrections are obtained by evaluating the right hand side of the equation below

$$H_2^{(1)F} = i[S_1, H_1^F] - \frac{1}{2}[S_1, [S_1, H_0^F]] = i[S_1, H_{1,\text{dia}}^F] + \frac{i}{2}[S_1, H_{1,\text{off-dia}}^F]. \quad (29)$$

In the above equation, the first expression results in operators that are off-diagonal in the Fourier dimension (i.e., $m \neq 0$) and has a minimal contribution to the overall spin dynamics. Hence, second-order corrections are confined only to the evaluation of the second term. The effective Hamiltonian describing the spin dynamics in R² experiments is

$$H_{\text{eff}}^F = H_0^F + H_{1,\text{dia}}^{(1)F} + H_{2,\text{dia}}^{(1)F} = \sum_{p=1}^4 \omega_p I^{p,p} + \sum_{p=1}^4 z_0^{p,p} Z_0^{p,p} + x_{12,0}^{2,3} X_0^{2,3} + iy_{12,0}^{2,3} Y_0^{2,3} + H_{2,\text{dia}}^{(1)F}, \quad (30)$$

which is in agreement with the descriptions presented in earlier reports. In Fig. 5, we present the simulation of the MAS spectrum at the R² condition and compare the spectrum with the dipolar-coupled spin pair. The observed broadening of the spectrum is in agreement with experiment and confirms the validity of the generalized effective Hamiltonian approach presented in the article. It is important to note here that the effective Hamiltonian for rotational resonance could well have been obtained by taking the $H_{1,\text{dia}}^F$ in H_0^F . Such an approach results in a set of coupled equations given below and complicates the procedure for evaluating the coefficients associated with the various operators in S_1 function¹² in the equation

$$H_1^{(1)F} = H_1^F + i[S_1, H_0^F] = H_{1,\text{dia}}^F. \quad (31)$$

This equation represents the following group of equations for the coefficients:

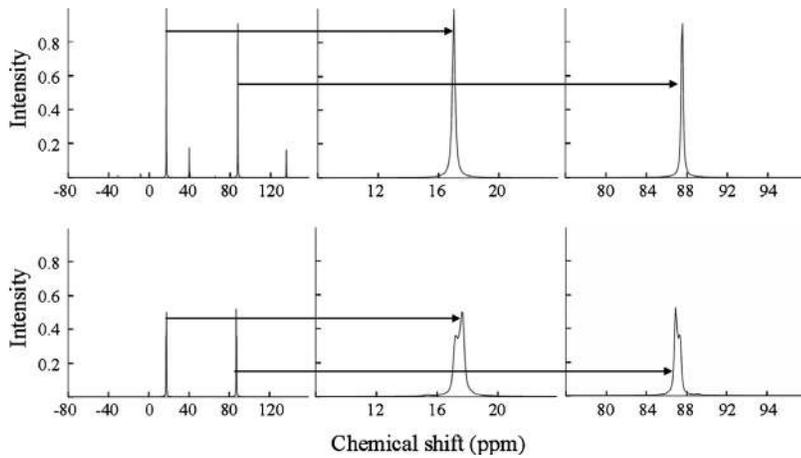


FIG. 5. Comparison of ^{13}C MAS spectrum for a dipolar-coupled spin-1/2 system (top panel) and the corresponding spectrum at the R^2 matching condition (lower panel). The spectrum at R^2 matching condition is broad due to the reintroduction of the dipolar interactions resulting in lower sensitivity. Input parameters employed for the simulation are similar to that used in Fig. 2.

$$z_m^{1,1} - A_m^{(1)} m \omega_r = 0,$$

$$z_m^{4,4} - A_m^{(4)} m \omega_r = 0,$$

$$z_m^{2,2} - A_m^{(2)} m \omega_r - C_{12,m}^{2,3} y_0^{2,3} + B_{12,m}^{2,3} x_0^{2,3} = 0,$$

$$z_m^{3,3} - A_m^{(3)} m \omega_r + C_{12,m}^{2,3} y_0^{2,3} - B_{12,m}^{2,3} x_0^{2,3} = 0,$$

$$x_{12,m}^{2,3} + C_{12,m}^{2,3} m \omega_r + \frac{1}{2}(A_m^{(3)} - A_m^{(2)}) y_{12,0}^{2,3} - \frac{1}{2}[z_0^{2,2} - z_0^{3,3}] B_{12,m}^{2,3} = 0,$$

$$y_{12,m}^{2,3} + B_{12,m}^{2,3} m \omega_r + \frac{1}{2}(A_m^{(3)} - A_m^{(2)}) x_{12,0}^{2,3} - \frac{1}{2}[z_0^{2,2} - z_0^{3,3}] C_{12,m}^{2,3} = 0.$$

Rather than solving these, the approach presented in Eqs. (27)–(29) is simpler and convenient for deriving effective Hamiltonians in recoupling experiments and can well be extended to multiple spins.

D. Effective Hamiltonians in quadrupolar spin systems

The Hamiltonian for a quadrupolar spin system ($I=1$) under MAS conditions is given by

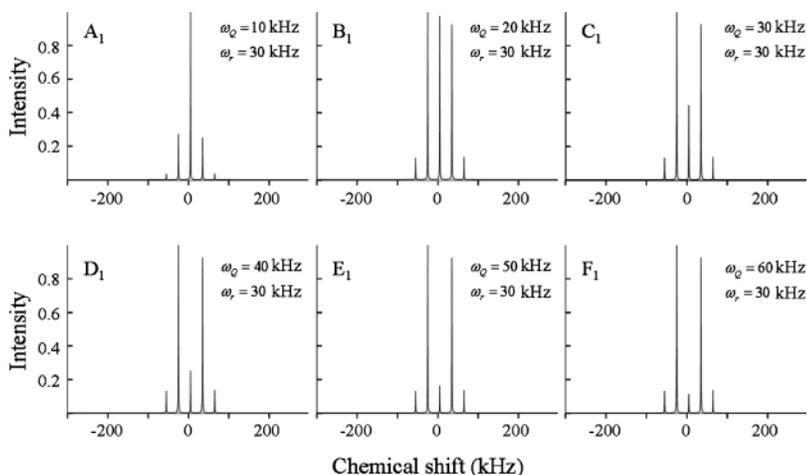


FIG. 6. A_1 , B_1 , C_1 , D_1 , E_1 , and F_1 represent simulated MAS spectra for a single spin-1 system obtained by varying the quadrupolar coupling strength keeping spinning frequency fixed. The following parameters were employed in the simulations: $\omega_1^{(0)} = 0.5$ kHz, $\delta_{1,\text{CSA}} = -3.38$ kHz, $\eta_{1,\text{CS}} = 0.99$, and $\eta_{1,Q} = 0$; CSA orientations α_{PM} , β_{PM} , and γ_{PM} are equal to 40° , 128° , and 122° , respectively. Quadrupolar orientations α_{PM}^Q , β_{PM}^Q , and γ_{PM}^Q equal to 30° , 60° , and 120° , respectively.

$$H(t) = \sum_{m=-2}^2 \omega^{(m)} e^{im\omega_r t} I_z + \sum_{\substack{m=-2, \\ m \neq 0}}^2 \omega_Q^{(m)} e^{im\omega_r t} [3I_z^2 - I^2]. \quad (33)$$

The corresponding Floquet transformation H^F is represented by

$$H^F = \sum_{p=1}^3 \omega_r I^{p,p} + \sum_{p=1}^3 z_0^{p,p} Z_0^{p,p} + \sum_{p=1}^3 \sum_{\substack{m=-2 \\ m \neq 0}}^2 z_m^{p,p} Z_m^{p,p}, \quad (34)$$

where the superscripts $p=1, 2$, and 3 denote the three-spin states $|1\rangle$, $|0\rangle$, and $|-1\rangle$, respectively. The constants associated with various operators in the Hamiltonian in Eq. (34) are given by

$$z_0^{1,1} = 2\omega_1^{(0)}, \quad z_0^{2,2} = 0, \quad z_0^{3,3} = -2\omega_1^{(0)},$$

$$z_m^{1,1} = 2\omega^{(m)} + 2\omega_Q^{(m)}, \quad z_m^{2,2} = -4\omega_Q^{(m)},$$

$$z_m^{3,3} = -2\omega^{(m)} + 2\omega_Q^{(m)}.$$

The subsequent description is identical to the single spin $I=1/2$ system and the MAS spectra are depicted in Figs. 6 and 7. In Fig. 6 are shown the ^2H MAS spectra for various quadrupolar coupling strengths from 10 to 60 kHz, at a fixed spinning frequency of 30 kHz (A_1 , B_1 , C_1 , D_1 , E_1 , and F_1). As the strength of the quadrupolar coupling increases, the

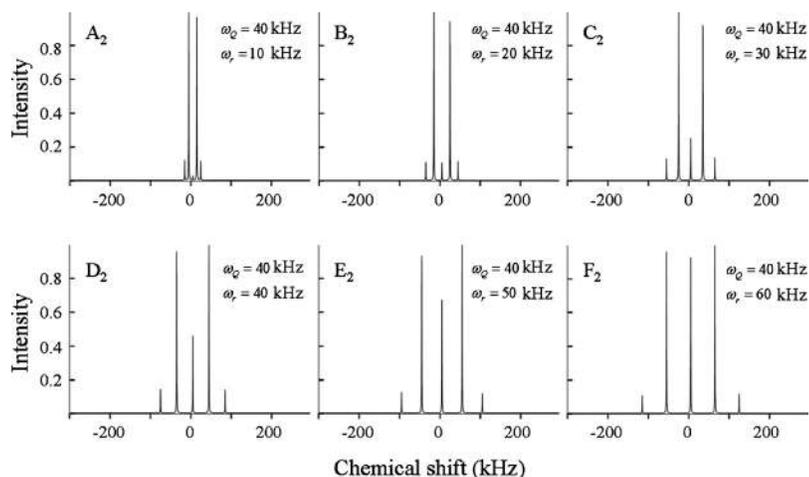


FIG. 7. A_2 , B_2 , C_2 , D_2 , E_2 , and F_2 represent simulated MAS spectra for a single spin-1 system obtained by varying spinning frequency keeping quadrupolar coupling strength fixed. Input parameters employed for the simulation are similar to that used in Fig. 6.

intensity of the central transition decreases. This trend is obvious from Fig. 7, where the spectra are compared at different spinning frequencies for a given quadrupolar coupling strength.

IV. CONCLUSIONS

In summary, the present study provides a generalized description of effective Floquet Hamiltonians for a system comprised of N -interacting spin systems including quadrupolar interactions. Attention is restricted to first-order quadrupolar interactions. The infinite dimensionality associated with conventional Floquet treatments is circumvented in our approach, thereby facilitating analytic treatments in terms of effective Hamiltonians derived from the contact transformation procedure. The generalized expressions for effective Hamiltonians presented here can be integrated with numerical methods for optimization and design of new NMR experiments and with the use of quadrupole interacting frames in the case of second-order and other quadrupole interactions.

ACKNOWLEDGMENTS

M.K.P. thanks the Department of Chemistry, Indian Institute of Technology Madras, Chennai, India for a fellowship that enabled him to carry out this work. M.S.K. thanks IIT Madras for financial support through its departmental grants and the Computer Centre of IIT Madras. The authors are grateful to Dr. Ramesh Ramachandran, Department of Chemistry, Indian Institute of Science Education and Research Mohali, India for valuable comments and suggestions.

¹P. Meakin and J. P. Jesson, *J. Magn. Reson.* (1969-1992) **10**, 290 (1973); **11**, 182 (1973); **13**, 354 (1974); **18**, 411 (1975).

²R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Clarendon, Oxford, 1987); N. Chandrakumar and S. Subramanian, *Modern Techniques in High Resolution in FT NMR* (Springer, New York, 1987); M. H. Levitt, *Spin Dynamics: Basics of Nuclear Magnetic Resonance* (Wiley, New York, 2001).

³S. A. Smith, T. O. Levante, B. H. Meier, and R. R. Ernst, *J. Magn. Reson.* **106A**, 75 (1994); M. Veshtort and R. G. Griffin, *ibid.* **178**, 248 (2006); M. Bak, J. T. Rasmussen, and N. C. Nielsen, *ibid.* **147**, 296 (2000).

⁴E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature (London)* **182**, 1659 (1958); I. J. Lowe, *Phys. Rev. Lett.* **2**, 285 (1959); M. Maricq and J. S. Waugh, *J. Chem. Phys.* **70**, 3300 (1979); M. Maricq, *Phys. Rev. B* **25**, 6622 (1982); M. Mehring, *High Resolution NMR in Solids* (Springer, New York, 1976); M. J. Duer, *Introduction to Solid State NMR Spectroscopy* (Blackwell, Oxford, 2004); B. C. Gerstein and C. Dybowski, *Transient Techniques in NMR of Solids* (Academic, San Diego, 1985); *NMR Spectroscopy of Biological Solids*, edited by A. Ramamoorthy (Taylor and Francis, New York, 2006).

⁵R. Ramesh and M. S. Krishnan, *J. Chem. Phys.* **114**, 5967 (2001); R. Ramachandran and R. G. Griffin, *ibid.* **122**, 164502 (2005).

⁶J. H. Shirley, *Phys. Rev. B* **138**, 979 (1965).

⁷Y. Zur, M. H. Levitt, and S. Vega, *J. Chem. Phys.* **78**, 5293 (1983); E. T. Olejniczak, S. Vega, and R. G. Griffin, *ibid.* **81**, 4804 (1984); E. M. Krauss and S. Vega, *Phys. Rev. A* **34**, 333 (1986); G. Goelman, D. B. Zax, and S. Vega, *J. Chem. Phys.* **87**, 31 (1987); A. Schmidt and S. Vega, *ibid.* **87**, 6895 (1987); D. B. Zax, G. Goelman, D. Abramovich, and S. Vega, *Adv. Magn. Reson.* **14**, 219 (1990); S. Vega, in *Nuclear Magnetic Probes for Molecular Dynamics*, edited by R. Tycko (Kluwer Academic, Amsterdam, 1994), p. 155; S. Vega, in *Encyclopedia of Nuclear Magnetic Resonance*, edited by D. M. Grant and R. K. Harris, (Wiley, New York, 1996), Vol. 3, p. 2011, and references therein; A. Schmidt and S. Vega, *J. Chem. Phys.* **96**, 2655 (1992); D. Abramovich and S. Vega, *J. Magn. Reson., Ser. A* **105**, 30 (1993); O. Weintraub and S. Vega, *J. Magn. Reson.* **109**, 14 (1994).

⁸T. O. Levante, M. Baldus, B. H. Meier, and R. R. Ernst, *Mol. Phys.* **86**, 1195 (1995); C. Filip, X. Filip, D. E. Demcos, and S. Hafner, *ibid.* **92**, 757 (1997); C. Filip, S. Hafner, I. Schnell, D. E. Demco, and H. W. Spiess, *J. Chem. Phys.* **110**, 423 (1999); A. Kubo and C. A. McDowell, *ibid.* **92**, 7156 (1990); T. Nakai and C. A. McDowell, *ibid.* **96**, 3452 (1992).

⁹M. J. Bayro, M. Huber, R. Ramachandran, T. C. Davenport, B. H. Meier, M. Ernst, and R. G. Griffin, *J. Chem. Phys.* **130**, 114506 (2009); R. Ramachandran, J. R. Lewandowski, P. C. A. van der Wel, and R. G. Griffin, *ibid.* **124**, 214107 (2006); R. Ramachandran and R. G. Griffin, *ibid.* **125**, 044510 (2006); R. Ramachandran, V. S. Bajaj, and R. G. Griffin, *ibid.* **122**, 164503 (2005).

¹⁰D. Papousek and M. R. Aliev, *Molecular Vibrational-Rotational Spectra* (Elsevier, Amsterdam, 1982); M. R. Aliev and V. T. Aleksanyan, *Opt. Spektrosk.* **24**, 520 (1968); **24**, 695 (1968); M. R. Aliev and J. K. G. Watson, in *Molecular Spectroscopy: Modern Research*, edited by K. Narahari Rao (Academic, New York, 1985), Vol. III, p. 1.

¹¹M. K. Pandey and R. Ramachandran, *Mol. Phys.* **108**, 619 (2010).

¹²U. Haeblerlen and J. S. Waugh, *Phys. Rev.* **175**, 453 (1968).