

Symmetry in the design of NMR multiple-pulse sequences

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The symmetry principles of NMR pulse-sequence design are summarized. The discussion is guided by an analogy with tiling schemes in the decorative arts. The symmetry operations for NMR pulse sequences are discussed in terms of excitation field modifiers and temporal modifiers. The quantum operators which describe the effect of these modifiers on the excitation field spin Hamiltonian are provided. The symmetry transformations of spin propagators, and the different types of pulse-sequence elements are discussed. The common types of symmetry expansion are treated using the propagator transformations and the Euler angles for the excitation field propagators. The selection rules associated with symmetrical pulse sequences are discussed using average Hamiltonian theory. © 2008 American Institute of Physics. [DOI: 10.1063/1.2831927]

I. INTRODUCTION

In NMR spectroscopy, the term *multiple-pulse sequence* usually refers to a dense, repetitive, sequence of radio-frequency pulses, or modulated radio-frequency fields, with a frequency close to the Larmor frequency of a nuclear spin isotope. The multiple-pulse sequence temporarily changes the evolution behavior of the nuclear spin system, sometimes mimicking the removal of some of the nuclear spin interactions, an effect that is called *decoupling*. The multiple-pulse sequence may also be synchronized with periodic mechanical manipulations, such as sample rotation. Sometimes the mechanical sample rotation decouples some of the nuclear spin interactions, but the multiple-pulse sequence restores some of them selectively. This is called *recoupling*.

The effective removal of a nuclear spin interaction by applying a resonant rf field was first observed by Sarles and Cotts in the case of sodium fluoride.¹ The ²³Na NMR resonance was narrowed by applying a rf field at the ¹⁹F Larmor frequency. *Heteronuclear decoupling* is now so familiar that one forgets how remarkable it is. It works because the magnetic interactions of the nuclei with applied fields are often stronger than the interactions of nuclei with their own molecular environment, including the interactions with neighboring nuclei.² This is a highly unusual situation which is almost specific to NMR spectroscopy, at least in routine contexts.

Homonuclear decoupling was first achieved by Lee and Goldburg,³ by using an off-resonance radio-frequency field. The frequency and amplitude of the rf field were adjusted so that the effective field in the rotating reference frame subtends the “magic angle” ($\arctan \sqrt{2}$) with the static magnetic field. This averages out interactions that are second rank with respect to spin rotations. The principles of magic-angle spinning, in which the spatial second-rank interactions are averaged out by mechanical rotation, had already been established by Lowe⁴ and by Andrew *et al.*⁵

The early methods involved simple, unmodulated, rf fields, and were not very efficient. The increasing availability of sufficiently fast and flexible radio-frequency hardware allowed the development of multiple-pulse schemes. Early attempts to optimize rf modulation schemes by examining their Fourier transforms led nowhere, since the nuclear spin response is not usually linear and is therefore only distantly related to the frequency spectrum of the excitation.

The average Hamiltonian theory (AHT) championed by Haeberlen and Waugh,⁶ and by Mansfield⁷ provided an appropriate theoretical framework for understanding the behavior of multiple-pulse sequences. This approach is still of central importance in theory of multiple-pulse NMR, despite the emergence of alternative methods such as the Floquet theory,^{8,9} the exact effective Hamiltonian theory,^{10,11} and the Fer expansion,¹² which have advantages in some circumstances. I will only use the AHT in this article.

The development of the AHT allowed the rational construction of multiple-pulse sequences for solid-state NMR. Symmetry arguments were immediately invoked to aid in the design. For example, so-called *symmetrization* of homonuclear decoupling pulse sequences was used to eliminate even-order average Hamiltonian correction terms (for the numbering scheme of the AHT terms, see below).^{6,7} This led to the construction of landmark sequences such as WAHUA (Refs. 6 and 13) and MREV8.^{7,14} Extensions of this approach led to complex high-performance supercycles such as BR24.¹⁵ Symmetry arguments were also used for the construction of pulse sequences for selective multiple-quantum excitation in solids and liquid crystals.^{16,17}

AHT was also applied in solution NMR to develop composite pulse sequences for broadband heteronuclear decoupling.^{18–22} The use of AHT superseded an earlier design principle, which employed the frequency spectrum of the excitation, a concept of little predictive value in the non-linear response regime. These pulse sequences were expanded into elaborate supercycles, again using transformations based on symmetry relationships.^{19,20,22–24}

The combination of magic-angle spinning with rotation-

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synchronized rf pulse sequences leads to many additional possibilities. The first recoupling experiment was probably performed by Yarim-Agaev *et al.*,²⁵ who applied rotation-synchronized rf pulses to restore the effect of the chemical shift anisotropy (CSA), which is normally averaged out by magic-angle spinning. However, the term “recoupling” first appeared in conjunction with the application of a rf field to restore the effect of heteronuclear dipole-dipole interactions.²⁶ A rich flora of rotation-synchronized multiple-pulse sequences now exist, for homonuclear recoupling,^{27–48} heteronuclear recoupling,^{26,49–55} CSA recoupling,^{25,56–60} homonuclear decoupling,^{3,6,7,13–15,61–66} heteronuclear decoupling,^{51–55,67–69} selection of scalar interactions,^{70–73} and for reconstructing the isotropic low-field form of the dipole-dipole Hamiltonian.^{74,75} Symmetry arguments have been used to construct many of these pulse sequences.

Many of the symmetry arguments used to construct rotor-synchronized pulse sequences have been codified in a set of common principles.⁷⁶ This has allowed a concise classification of many existing sequences as well as guiding the construction of many new ones. The symmetries of many single-channel pulse sequences are denoted using the symbols CN_n^ν and RN_n^ν , where the letter C or R is used as a code for the type of building block used to construct the sequence, and the numbers N , n , and ν are integers known as *symmetry numbers*. This notation is explained below.

Although much previous work in NMR pulse-sequence design has made extensive use of pulse-sequence symmetry, there have been few attempts to link this *dynamic* symmetry with the *spatial* symmetries involved in the decorative arts and in crystallography.⁷⁷ The following section develops the analogy between NMR and symmetrical decorative patterns by considering a simple one-dimensional form of spatial symmetry.

It is not practical to cover the symmetry principles underlying all NMR multiple-pulse sequences in a single article. The discussion below covers a few of the salient points, highlighting the relationships and commonalities between several different types of pulse sequence.

II. SPATIAL SYMMETRY

An object is said to be symmetric with respect to a given operation if it does not change when that operation is applied.

The most familiar type is spatial symmetry. This can involve spatial rotations or spatial translations, or combinations of both. For example, a sphere is symmetric with respect to all three-dimensional rotations, while an equilateral triangle is symmetric with respect to rotations through multiples of $2\pi/3$ radians about a perpendicular axis passing through its center.

In the decorative arts, operations such as color transformations may be involved as well as translations, reflections, and rotations. Such symmetries are related to those involved in NMR pulse-sequence design and worth looking at closely.

Figure 1 shows arrangements of square patterned tiles arranged along the x -axis, each with sides of length L . Suppose that the tiles are indexed by an integer $p \in \{0, 1, \dots\}$,

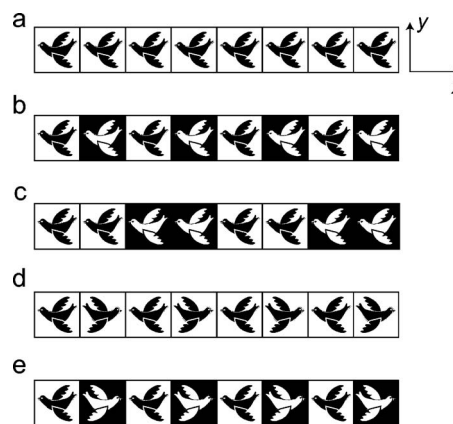


FIG. 1. Some one-dimensional tiling schemes. (a) Repetitive translation of a tile; (b) translation combined with color alternation; (c) pairs of tiles with alternating colors; (d) alternate reflections; (e) reflections combined with color alternation.

and the color at a point with coordinates $\mathbf{r}=(x,y)$ is denoted $C(\mathbf{r})$. Denote a general point within the first tile ($p=0$) by $\mathbf{r}_0=(x_0,y_0)$, and a symmetry-related point within the p th tile by $\mathbf{r}_p=(x_p,y_p)$. In general, any symmetry-related pair of points is related by a symmetry operation \hat{S}_p , which depends only on the index p and the decorative design, i.e.,

$$\mathbf{r}_p = \hat{S}_p \mathbf{r}_0. \quad (1)$$

The designs in Fig. 1 use only two spatial operators \hat{S}_p : the spatial translation operator \hat{X}_p , which generates a shift along the x -axis,

$$\hat{X}_p \mathbf{r} = \mathbf{r} + pL\mathbf{e}_x \quad (2)$$

and the reflection operator $\hat{\sigma}$, which generates a *reflection* in a vertical plane passing through the center of the tile as follows:

$$\hat{\sigma}(x,y) = (L-x,y). \quad (3)$$

This assumes that the left-hand edge of the first tile is at the origin of the x -axis.

Each tiling scheme in Fig. 1 is defined by a relationship of the form

$$C(\mathbf{r}_p) = \hat{C}_p(C(\mathbf{r}_0)), \quad (4)$$

where \hat{C}_p is an operator that modifies the color of the point to which it is applied. The designs in Fig. 1 employ only two color operators: The operator \hat{C}_{same} , which leaves the color unchanged, or the operator \hat{C}_{opp} , which exchanges black and white,

$$\hat{C}_{\text{same}}(\text{B}) = \text{B}, \quad \hat{C}_{\text{same}}(\text{W}) = \text{W},$$

$$\hat{C}_{\text{opp}}(\text{B}) = \text{W}, \quad \hat{C}_{\text{opp}}(\text{W}) = \text{B},$$

where B indicates black and W indicates white.

Equation (4) is the mathematical expression of a *symmetry relationship*, since it defines a condition of invariance with respect to combinations of spatial symmetry operations

(encoded in the operators \hat{S}_p) and color-change operations (encoded in the operators \hat{C}_p).

The patterns shown in Fig. 1 are periodic, although Eq. (4) also allows aperiodic symmetries, as discussed below. If the number of tiles in a period is denoted P , then the operators \hat{C}_p and \hat{S}_p have the following property:

$$\begin{aligned}\hat{C}_{p+KP} &= \hat{C}_p, \\ \hat{S}_{p+KP} &= \hat{X}_p^{KP} \hat{S}_p,\end{aligned}\quad (5)$$

where K is an integer. A periodic pattern with period P therefore requires the definition of P spatial operators $\{\hat{S}_0, \hat{S}_1, \dots, \hat{S}_{P-1}\}$ and P color operators $\{\hat{C}_0, \hat{C}_1, \dots, \hat{C}_{P-1}\}$.

The pattern in Fig. 1(a) involves a simple translation (period $N=1$) and the trivial color and spatial operators as follows:

$$\hat{S}_0 = \hat{X}_0, \quad \hat{C}_0 = \hat{C}_{\text{same}}, \quad (6)$$

where \hat{X}_0 is the spatial identity operator: $\hat{X}_0 \mathbf{r} = \mathbf{r}$. From Eq. (5) and $N=1$, Eq. (6) leads to the operators for all tiles as follows:

$$\begin{aligned}\hat{S}_1 &= \hat{X}_1, \quad \hat{C}_1 = \hat{C}_{\text{same}}, \\ \hat{S}_2 &= \hat{X}_2, \quad \hat{C}_2 = \hat{C}_{\text{same}}, \\ &\vdots, \quad \vdots.\end{aligned}$$

The pattern in Fig. 1(b), on the other hand, has a period $N=2$ and involves exchange of colors on alternating tiles as follows:

$$\begin{aligned}\hat{S}_0 &= \hat{X}_0, \quad \hat{C}_0 = \hat{C}_{\text{same}}, \\ \hat{S}_1 &= \hat{X}_1, \quad \hat{C}_1 = \hat{C}_{\text{opp}},\end{aligned}$$

leading through Eq. (5) to the further operators

$$\begin{aligned}\hat{S}_2 &= \hat{X}_2, \quad \hat{C}_2 = \hat{C}_{\text{same}}, \\ \hat{S}_3 &= \hat{X}_3, \quad \hat{C}_3 = \hat{C}_{\text{opp}}, \\ &\vdots, \quad \vdots.\end{aligned}$$

The pattern in Fig. 1(c) has a period $N=4$ as follows:

$$\begin{aligned}\hat{S}_0 &= \hat{X}_0, \quad \hat{C}_0 = \hat{C}_{\text{same}}, \\ \hat{S}_1 &= \hat{X}_1, \quad \hat{C}_1 = \hat{C}_{\text{same}}, \\ \hat{S}_2 &= \hat{X}_2, \quad \hat{C}_2 = \hat{C}_{\text{opp}}, \\ \hat{S}_3 &= \hat{X}_3, \quad \hat{C}_3 = \hat{C}_{\text{opp}}.\end{aligned}$$

The patterns in Figs. 1(d) and 1(e) both have a period $N=2$ and involve reflections as well as translations. The pattern in Fig. 1(d) is defined by the operator set

$$\hat{S}_0 = \hat{X}_0, \quad \hat{C}_0 = \hat{C}_{\text{same}},$$

$$\hat{S}_1 = \hat{X}_1 \hat{\sigma}, \quad \hat{C}_1 = \hat{C}_{\text{same}},$$

while the pattern in Fig. 1(e) is defined by the operator set

$$\hat{S}_0 = \hat{X}_0, \quad \hat{C}_0 = \hat{C}_{\text{same}},$$

$$\hat{S}_1 = \hat{X}_1 \hat{\sigma}, \quad \hat{C}_1 = \hat{C}_{\text{opp}}.$$

III. PULSE SEQUENCES

NMR pulse sequences resemble one-dimensional tiling schemes. The pulses are arranged along the time axis, i.e., in chronological order, rather than being lined up along a spatial axis. The rf pulse parameters (radio-frequency field amplitudes, phases, and frequencies) play an analogous role to the tile colors.

A. Modulated excitation fields

In NMR, a sample is exposed to one or more transverse radio-frequency fields, and a longitudinal field with a large static component as well as relatively small modulated components, which are used, for example, in NMR imaging. In general, the amplitude, frequency, and phase of the radio-frequency field, and the variable component of the longitudinal field, may be modulated in time. The total magnetic field may be written in the fixed (laboratory) frame as follows:

$$\mathbf{B}^{\text{lab}}(t) = B^0 \mathbf{e}_z + \mathbf{B}_e^{\text{lab}}(t), \quad (7)$$

where B^0 is the static field, and the modulated excitation field is defined in the lab frame by

$$\mathbf{B}_e^{\text{lab}}(t) = B_z(t) \mathbf{e}_z + B_{\text{rf}}(t) \cos(\omega_{\text{rf}}^{\text{lab}}(t)t + \phi_{\text{rf}}(t)) \mathbf{e}_x. \quad (8)$$

Here $B_z(t)$ and $B_{\text{rf}}(t)$ are the amplitudes of the modulated longitudinal and transverse fields. The term ϕ_{rf} is the phase of the radio-frequency field, while $\omega_{\text{rf}}^{\text{lab}}$ is the frequency of the rf field, as seen from the laboratory reference frame. In general, $B_z(t)$, $B_{\text{rf}}(t)$, $\omega_{\text{rf}}(t)$, and $\phi_{\text{rf}}(t)$ are all time dependent.

It is convenient to write the spin Hamiltonian in a frame rotating at the spectrometer reference frequency ω_{ref} , which is close to the nuclear Larmor frequency. This rotating-frame Hamiltonian may be written as follows:

$$\mathcal{H}(t) = \mathcal{H}_i(t) + \mathcal{H}_e(t), \quad (9)$$

where \mathcal{H}_i describes the internal interactions of the nuclear spins with their microscopic surroundings and \mathcal{H}_e describes the interaction with the modulated excitation field. If rapidly oscillating terms are neglected, the rotating-frame excitation Hamiltonian is given by

$$\mathcal{H}_e(t) = \boldsymbol{\omega}(t) \cdot \mathbf{I} = \omega_x I_x + \omega_y I_y + \omega_z I_z, \quad (10)$$

where

$$\boldsymbol{\omega}(t) = \begin{pmatrix} \omega_x(t) \\ \omega_y(t) \\ \omega_z(t) \end{pmatrix}. \quad (11)$$

The Cartesian components of the rotating-frame excitation field, expressed as frequencies, are given by

$$\begin{aligned} \omega_x(t) &= \omega_{\text{nut}}(t) \cos \phi_{\text{rf}}(t), \\ \omega_y(t) &= \omega_{\text{nut}}(t) \sin \phi_{\text{rf}}(t), \\ \omega_z(t) &= -\gamma B_z(t) + \omega_{\text{rf}}(t) - \omega_{\text{ref}}, \end{aligned} \quad (12)$$

where the nutation frequency, which expresses the strength of the rf field, is given by

$$\omega_{\text{nut}}(t) = \left| \frac{1}{2} \gamma B_{\text{rf}}(t) \right|. \quad (13)$$

Here γ is the gyromagnetic ratio of the resonant nuclei. The nutation frequency ω_{nut} may be varied by modulating the amplitude of the applied rf field. The longitudinal component of the excitation field is expressed as the frequency ω_z and may be changed either by varying the longitudinal magnetic field, or by changing the irradiation frequency. For single-channel sequences, these effects are equivalent, except for a change in sign.

These equations assume that the implementation of any discontinuous frequency jumps in ω_{ref} is *phase continuous*.⁶² This is the usual case for modern rf modulation hardware.

The rotating-frame excitation Hamiltonian in Eq. (10) may also be written as

$$\mathcal{H}_e = \omega_{\text{eff}} R_z(\phi_{\text{rf}}) R_y(\theta_{\text{eff}}) I_z R_y(\theta_{\text{eff}})^\dagger R_z(\phi_{\text{rf}})^\dagger, \quad (14)$$

where the magnitude of the effective field and its tilt angle are given by

$$|\omega_{\text{eff}}|^2 = |\omega_{\text{nut}}|^2 + |\omega_z|^2, \quad (15)$$

$$\tan \theta_{\text{eff}} = \omega_{\text{nut}} / \omega_z,$$

and the rotation operators are defined

$$R_\mu(\phi) = \exp\{-i\phi I_\mu\}, \quad (16)$$

with $\mu \in \{x, y, z\}$.

B. Pulse-sequence notation

In many cases the excitation field modulation is piecewise time independent, within hardware limitations.

Consider a pulse sequence \mathcal{S} composed of N_S pulses with durations $\{\tau_0, \tau_1 \cdots \tau_{N_S-1}\}$. If the pulse sequence starts at time point t^0 , the initial time points of each pulse in the sequence are given by the recursion

$$t_{p+1}^0 = t_p^0 + \tau_p, \quad (17)$$

where $t_0^0 = t^0$. All components of the modulation field are piecewise time independent as follows:

$$\boldsymbol{\omega}(t) = \boldsymbol{\omega}_p \quad \text{for } t_p^0 \leq t \leq t_{p+1}^0, \quad (18)$$

where $p \in \{0, 1, \cdots, N_S-1\}$. The total duration of the sequence is given by

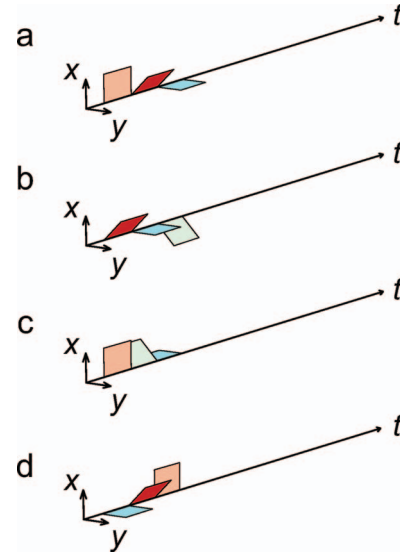


FIG. 2. (Color) The effect of four different pulse sequence modifiers on the sequence $90_0 90_{45} 90_{90}$. (a) The identity operator \hat{E} ; (b) the phase shift modifier $\hat{\Phi}(\pi/4)$; (c) the xz -reflection modifier $\hat{\sigma}_{xz}$; (d) the order-reversal operator \hat{O}_{rev} .

$$\tau_{\mathcal{S}} = \sum_{p=0}^{N_S-1} \tau_p. \quad (19)$$

If the amplitude and frequency of the rf field are constant during the pulse sequence, so that only the phase changes, and no modulated longitudinal fields are used, the conventional notation for the pulse sequence is as follows:

$$\mathcal{S} = (\beta_0)_\phi (\beta_1)_{\phi_1} \cdots (\beta_{N_S-1})_{\phi_{N_S-1}}. \quad (20)$$

The flip angles β_p are defined in terms of the modulation field components and the pulse durations τ_p through

$$\beta_p = |\omega_{\text{eff}}| \tau_p. \quad (21)$$

In this article, flip angles and phases are specified in degrees when using the notation in Eq. (20). By definition, contiguous pulses with the same phase may be combined by adding up the flip angles as follows:

$$\{\cdots (\beta_1)_\phi (\beta_2)_\phi \cdots\} = \{\cdots (\beta_1 + \beta_2)_\phi \cdots\}. \quad (22)$$

All phases are periodic, modulo 2π .

A graphical representation of the fixed-frequency pulse sequence $90_0 90_{45} 90_{90}$ is shown in Fig. 2(a). In this representation, the pulse sequence is drawn as a set of rectangles arranged along the time axis, with the direction of the rectangle in the xy -plane representing the phase of the rf field.

Some pulse sequences use a modulation of the rf, or a change in sign of the modulated longitudinal field, to change the sign of the component ω_z during the pulse sequence. In this case, the pulse sequences are noted as follows:

$$\mathcal{S} = \cdots (\beta_\phi)^+ \cdots (\beta')_\phi^- \cdots, \quad (23)$$

where the superscripts indicate the sign of ω_z during the pulse.

C. Excitation field Hamiltonians and propagators

The excitation field Hamiltonian generates an evolution of spin states $|\psi\rangle$, which may be written as

$$|\psi\rangle(t) = U_e(t, 0)|\psi\rangle(0), \quad (24)$$

where the propagation operator solves the differential equation

$$\frac{d}{dt}U_e(t, 0) = -i\mathcal{H}_e(t)U_e(t, 0) \quad (25)$$

and the boundary condition

$$U_e(0, 0) = 1. \quad (26)$$

The general solution of Eqs. (25) and (26) may be written as follows:⁷⁸

$$U_e(t, 0) = \lim_{\delta t \rightarrow 0} \exp\{-i\mathcal{H}_e(t)\delta t\} \cdots \exp\{-i\mathcal{H}_e(\delta t)\delta t\} \times \exp\{-i\mathcal{H}_e(0)\delta t\}, \quad (27)$$

where the product of exponential operators is chronologically ordered from right to left. In the case of a piecewise time-independent Hamiltonian, as encountered for discrete rectangular pulses, the solution is as follows:

$$U_e(t_p, 0) = \exp\{-i\mathcal{H}_p^e(t_p - t_p^0)\}U_{p-1}^e \cdots U_1^eU_0^e, \quad (28)$$

where U_p^e is the rf propagator for the p th pulse as follows:

$$U_p^e = R_z(\phi_p)R_y(\theta_p^{\text{eff}})R_z(\omega_p^{\text{eff}}\tau_p)R_y(\theta_p^{\text{eff}})^\dagger R_z(\phi_p)^\dagger \quad (29)$$

and $t_p^0 \leq t_p \leq t_{p+1}^0$.

Since Eq. (10) contains a linear combination of angular momentum operators, the propagator may always be expressed as a rotation operator in three-dimensional space. This rotation may be parametrized using three Euler angles as follows:

$$U_e(t, 0) = R_z(\alpha_e(t))R_y(\beta_e(t))R_z(\gamma_e(t)). \quad (30)$$

The symbol Ω_e is used to indicate the set of three Euler angles, $\Omega_e = \{\alpha_e, \beta_e, \gamma_e\}$. As the pulse sequence proceeds, the three Euler angles $\Omega_e(t)$ vary in time, according to the solution of the differential equation (25) under the sequence of modulation fields defined by $\omega(t)$.

The overall propagator generated by the excitation field over the complete sequence is denoted as follows:

$$U_e(S) = U_e(\tau_S, 0). \quad (31)$$

Similarly, the Euler angles describing the rotation induced by the excitation field over the complete sequence S are denoted by

$$\alpha_e(\tau_S, 0) = \alpha_e(S),$$

$$\beta_e(\tau_S, 0) = \beta_e(S), \quad (32)$$

$$\gamma_e(\tau_S, 0) = \gamma_e(S).$$

D. Pulse-sequence modifiers

It is convenient to introduce a set of *pulse-sequence modifiers* which change the excitation field sequence according to fixed rules. These modifiers may involve either the excitation fields (called *excitation field modifiers*) or the order of the pulse-sequence elements in time (called *temporal modifiers*). In general, the generation of a new pulse sequence S' by modifying a pulse sequence S is denoted as

$$S' = \hat{\mathbb{F}}\hat{\mathbb{T}} \cdot S, \quad (33)$$

where $\hat{\mathbb{F}}$ is an excitation field modifier and $\hat{\mathbb{T}}$ is a temporal modifier. The excitation field and temporal modifiers commute ($\hat{\mathbb{F}}\hat{\mathbb{T}} = \hat{\mathbb{T}}\hat{\mathbb{F}}$).

1. Excitation field modifiers

The excitation field modifiers $\hat{\mathbb{F}}$ play an analogous role to the color operators used to describe the symmetries of decorative tiling schemes.

The relevant modifiers are as follows

- (1) The *identity modifier* \hat{E} leaves the excitation field parameters unchanged as follows:

$$\hat{E} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} = \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}. \quad (34)$$

- (2) The *phase shift modifier* $\hat{\Phi}(\phi)$ changes the phase of the rf field by ϕ , leaving the frequency and amplitude unchanged. This rotates the excitation field about the z -axis as follows:

$$\hat{\Phi}(\phi) \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} = \begin{pmatrix} \omega_x \cos \phi - \omega_y \sin \phi \\ \omega_x \sin \phi + \omega_y \cos \phi \\ \omega_z \end{pmatrix}. \quad (35)$$

- (3) The *xz-reflection modifier* $\hat{\sigma}_{xz}$ reflects the excitation field in the xz -plane as follows:

$$\hat{\sigma}_{xz} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} = \begin{pmatrix} \omega_x \\ -\omega_y \\ \omega_z \end{pmatrix}. \quad (36)$$

This modifier is implemented by changing the *sign* of all phases, leaving the amplitude and frequency unchanged.

- (4) The *xy-reflection modifier* $\hat{\sigma}_{xy}$ reflects the excitation field in the xy -plane as follows:

$$\hat{\sigma}_{xy} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} = \begin{pmatrix} \omega_x \\ \omega_y \\ -\omega_z \end{pmatrix}. \quad (37)$$

In general, this modifier is implemented by changing the sign of the rf relative to the reference frequency, as well as the sign of the modulated longitudinal field.

The modifier $\hat{\Phi}(0)$ is equivalent to the identity \hat{E} . All pairs of modifiers commute, with the exception of $\hat{\Phi}$ and $\hat{\sigma}_{xz}$, for which $\hat{\Phi}(\phi)\hat{\sigma}_{xz} = \hat{\sigma}_{xz}\hat{\Phi}(-\phi)$.

The application of the same excitation field modifier \hat{F} to all time points of a pulse sequence \mathcal{S} , without changing the sequence of elements in time, is denoted as follows:

$$\mathcal{S}' = \hat{F} \cdot \mathcal{S}. \quad (38)$$

Some examples are as follows:

$$\begin{aligned} \hat{E} \cdot 90_{90}180_0 &= 90_{90}180_0, \\ \hat{\Phi}(\pi/2) \cdot 90_{90}180_0 &= 90_{180}180_{90}, \\ \hat{\sigma}_{xz} \cdot 90_{90}180_0 &= 90_{-90}180_0, \\ \hat{\sigma}_{xy} \cdot 90_{90}^+180_0^- &= 90_{90}^-180_0^+. \end{aligned} \quad (39)$$

Rf field modifications are analogous to changing the color scheme of a tile, according to a fixed set of rules, as illustrated by the first three patterns in Fig. 1.

Figure 2 provides a graphical representation of the excitation field modifiers. Figure 2(b) shows that applying the phase shift operator $\hat{\Phi}(\pi/4)$ to $90_090_{45}90_{90}$ generates $90_{45}90_{90}90_{135}$. Note the rotation of the pattern around the time axis. Figure 2(c) shows the effect of $\hat{\sigma}_{xz}$ on $90_090_{45}90_{90}$. The sequence is reflected in the xz -plane, leading to $90_090_{-45}90_{-90}$.

2. Temporal modifiers

A pulse sequence may also be modified by changing the order of its elements in time. The relevant temporal modifiers \hat{T} are as follows.

- (1) *Order reversal*. The operator \hat{O}_{rev} reverses the order of the pulse-sequence elements in time, for example,

$$\hat{O}_{\text{rev}} \cdot 90_{90}180_0 = 180_090_{90}, \quad (40)$$

$$\hat{O}_{\text{rev}} \cdot 90_{90}^+180_0^- = 180_0^-90_{90}^+.$$

Figure 2(d) shows the effect of order reversal on the pulse sequence $90_090_{45}90_{90}$. The order reversal operator \hat{O}_{rev} plays a similar role for a pulse sequence as the reflection operator $\hat{\sigma}$ does for a tile, see Eq. (3).

- (2) *Cyclic permutation*. Pulse sequences may also be modified by cyclic permutations of one or more elements.

The *forward cyclic permutation operator* $\hat{P}^+(\mathcal{E})$ deletes the element \mathcal{E} from the front of a pulse sequence and moves it to the back, for example,

$$\hat{P}^+(45_{90}) \cdot 90_{90}180_0 = 45_{90}180_045_{90}. \quad (41)$$

The *backward cyclic permutation operator* $\hat{P}^-(\mathcal{E})$ deletes the element \mathcal{E} from the end of a pulse sequence and moves it to the front, for example,

$$\hat{P}^-(90_0) \cdot 90_{90}180_0 = 90_090_{90}90_0. \quad (42)$$

Clearly, the forward cyclic permutation $\hat{P}^+(\mathcal{E}) \cdot \mathcal{S}$ is only defined if the sequence \mathcal{S} begins with the element \mathcal{E} , and the backward cyclic permutation $\hat{P}^-(\mathcal{E}) \cdot \mathcal{S}$ is only defined if the sequence \mathcal{S} ends with the element \mathcal{E} .

E. Hamiltonian transformations

The modification of a pulse sequence changes the excitation Hamiltonian according to defined rules. The general form of this transformation is as follows:

$$\mathcal{S}' = \hat{F}\hat{T} \cdot \mathcal{S}: \quad \mathcal{H}'_e(t) = \hat{H}_F \mathcal{H}_e(\hat{T}t), \quad (43)$$

where \hat{H}_F is a superoperator, defining the effect of the excitation field modifier \hat{F} on the excitation Hamiltonian \mathcal{H}_e , while the operator \hat{T} describes the effect of the temporal modifier \hat{T} on the time coordinate t .

In general, the superoperator \hat{H}_F has the following effect when applied to an arbitrary operator Q :

$$\hat{H}_F Q = H_F Q H_F^\dagger, \quad (44)$$

where the spin operator H_F depends on the modifier \hat{F} .

1. Radio-frequency field modifiers

The operators H_F corresponding to the four common field modifiers \hat{F} are as follows:

$$\begin{aligned} \hat{F} = \hat{E}: \quad H_F &= 1, \\ \hat{F} = \hat{\Phi}(\phi): \quad H_F &= R_z(\phi), \\ \hat{F} = \hat{\sigma}_{xz}: \quad H_F &= R_y(\pi)\hat{K}, \\ \hat{F} = \hat{\sigma}_{xy}: \quad H_F &= R_z(\pi)\hat{K}. \end{aligned} \quad (45)$$

Here \hat{K} is the antilinear *time-reversal operator*,^{79,80} defined through the following properties:

$$\begin{aligned} \hat{K}I_\mu\hat{K}^\dagger &= -I_\mu, \\ \hat{K}i\hat{K}^\dagger &= -i. \end{aligned} \quad (46)$$

If several rf field operators are applied at the same time, the product of the corresponding operators H_F is taken, for example,

$$\begin{aligned} \hat{F} = \hat{\sigma}_{xy}\hat{\sigma}_{xz}: \quad H_F &= R_z(\pi)\hat{K} \cdot R_y(\pi)\hat{K} \\ &= R_z(\pi)R_y(\pi) = R_x(-\pi). \end{aligned} \quad (47)$$

This shows that the combined effect of changing the sign of rf phases (represented by $\hat{\sigma}_{xz}$) and the sign of the offset frequency (represented by $\hat{\sigma}_{xy}$) is a rotation of the excitation field about the x -axis by the angle π .

The rf field modifiers may therefore be classified accord-

ing to whether they lead to *linear* or *antilinear* operators H_F as follows.

- (1) *Linear operators.* The following excitation field modifiers lead to *linear* Hamiltonian transformations: \hat{E} , $\hat{\Phi}$, and the product $\hat{\sigma}_{xz}\hat{\sigma}_{xy}$.
- (2) *Antilinear operators.* The following excitation field modifiers lead to *antilinear* Hamiltonian transformations: $\hat{\sigma}_{xz}$, $\hat{\sigma}_{xy}$, and the products $\hat{\sigma}_{xz}\hat{\Phi}$ and $\hat{\sigma}_{xy}\hat{\Phi}$.

2. Temporal modifiers

The operator \hat{T} describes the effect of the temporal modifier $\hat{\mathbb{T}}$ on the time coordinate.

- (1) In the case of the order-reversal operator $\hat{\mathbb{O}}_{\text{rev}}$, the temporal operator has the following effect:

$$\hat{\mathbb{T}} = \hat{\mathbb{O}}_{\text{rev}}: \quad \hat{T} = \hat{T}_{\text{rev}}, \quad (48)$$

where

$$\hat{T}_{\text{rev}}t = \tau_S - t \quad (49)$$

and τ_S is the duration of the pulse sequence.

- (2) In the case of the forward cyclic permutation modifier, the temporal operator has the following effect:

$$\hat{\mathbb{T}} = \hat{\mathbb{P}}^+(\mathcal{E}): \quad \hat{T}t = \begin{cases} t + \tau_E, & 0 \leq t \leq \tau_S - \tau_E \\ t - \tau_S + \tau_E, & \tau_S - \tau_E \leq t \leq \tau_S, \end{cases} \quad (50)$$

where τ_E is the duration of the permuted element.

- (3) In the case of the backward cyclic permutation modifier, the temporal operator is instead as follows:

$$\hat{\mathbb{T}} = \hat{\mathbb{P}}^-(\mathcal{E}): \quad \hat{T}t = \begin{cases} t + \tau_S - \tau_E, & 0 \leq t \leq \tau_E \\ t - \tau_E, & \tau_E \leq t \leq \tau_S. \end{cases} \quad (51)$$

F. Propagator transformations

Now consider the effect of the sequence modifiers on the propagator $U_e(t, 0)$ induced by the excitation field from the time origin $t=0$ up to a general time point t . In the discussion below, a general linear transformation operator for the excitation Hamiltonian is denoted \hat{L}_F , while a general antilinear transformation operator for the excitation Hamiltonian is denoted \hat{A}_F .

1. Linear transformations

Consider the case where a pulse-sequence modification involves a linear transformation of the excitation Hamiltonian ($H_F = \hat{L}_F H_F$), but no temporal modification. The effect of the excitation modification on the excitation propagator is readily calculated as follows:⁷⁸

$$S' = \hat{\mathbb{F}} \cdot S:$$

$$\begin{aligned} U'_e(t, 0) &= \lim_{\delta t \rightarrow 0} \exp\{-i\mathcal{H}'_e(t)\delta t\} \cdots \exp\{-i\mathcal{H}'_e(0)\delta t\} \\ &= \lim_{\delta t \rightarrow 0} \exp\{-i\hat{L}_F \mathcal{H}_e(t) \hat{L}_F^\dagger \delta t\} \cdots \\ &\quad \times \exp\{-i\hat{L}_F \mathcal{H}_e(0) \hat{L}_F^\dagger \delta t\} \\ &= \hat{L}_F \left\{ \lim_{\delta t \rightarrow 0} \exp\{-i\mathcal{H}_e(t)\delta t\} \cdots \right. \\ &\quad \times \exp\{-i\mathcal{H}_e(0)\delta t\} \left. \right\} \hat{L}_F^\dagger = \hat{L}_F U_e(t, 0) \hat{L}_F^\dagger, \end{aligned} \quad (52)$$

where \hat{L}_F indicates a linear operator. When an excitation field transformation corresponds to a linear transformation of the excitation Hamiltonian, then the propagator is subjected to the same linear transformation.

An example is provided by an overall phase shift applied to a pulse-sequence element. The propagator up to any time point is transformed as follows:

$$S' = \hat{\Phi}(\phi) \cdot S: \quad U'_e(t, 0) = R_z(\phi) U_e(t, 0) R_z(\phi)^\dagger. \quad (53)$$

The corresponding excitation Euler angles are therefore given by

$$S' = \hat{\Phi}(\phi) \cdot S: \quad \begin{cases} \alpha'_e(t) = \alpha_e(t) + \phi \\ \beta'_j(t) = \beta_c(t) \\ \gamma'_e(t) = \gamma_e(t) - \phi. \end{cases} \quad (54)$$

Similarly, the effect of a simultaneous phase and frequency inversion of a pulse sequence is as follows:

$$S' = \hat{\sigma}_{xz} \hat{\sigma}_{xy} \cdot S: \quad U'_e(t, 0) = R_x(-\pi) U_e(t, 0) R_x(-\pi)^\dagger, \quad (55)$$

leading to a change in sign of all excitation Euler angles:

$$S' = \hat{\sigma}_{xz} \hat{\sigma}_{xy} \cdot S: \quad \begin{cases} \alpha'_e(t) = -\alpha_e(t) \\ \beta'_e(t) = -\beta_e(t) \\ \gamma'_e(t) = -\gamma_e(t). \end{cases} \quad (56)$$

2. Antilinear transformations and order reversal

If the transformation of a pulse sequence falls into the *antilinear* category, useful expressions for the propagator are obtained if the antilinear excitation field modification is combined with reversal of the pulse-sequence order. The general result is as follows:⁷⁸

$$\begin{aligned} S' &= \hat{\mathbb{O}}_{\text{rev}} \hat{\mathbb{F}} \cdot S: \\ U'_e(t, 0) &= \lim_{\delta t \rightarrow 0} \exp\{-i\mathcal{H}'_e(t)\delta t\} \cdots \exp\{i\mathcal{H}'_e(0)\delta t\} \\ &= \lim_{\delta t \rightarrow 0} \exp\{-i\hat{A}_F \mathcal{H}_e(\tau_S - t) \hat{A}_F^\dagger \delta t\} \cdots \\ &\quad \times \exp\{-i\hat{A}_F \mathcal{H}_e(\tau_S) \hat{A}_F^\dagger \delta t\} \\ &= \hat{A}_F \left\{ \lim_{\delta t \rightarrow 0} \exp\{+i\mathcal{H}_e(\tau_S - t)\delta t\} \cdots \right. \\ &\quad \times \exp\{+i\mathcal{H}_e(\tau_S)\delta t\} \left. \right\} \hat{A}_F^\dagger \end{aligned}$$

$$\begin{aligned}
&= \hat{A}_F \left\{ \lim_{\delta t \rightarrow 0} \exp[-i\mathcal{H}_e(\tau_S)\delta t] \cdots \right. \\
&\quad \times \exp[-i\mathcal{H}_e(\tau_S - t)\delta t] \left. \right\}^\dagger \hat{A}_F^\dagger \\
&= \hat{A}_F U_e(\tau_S, \tau_S - t)^\dagger \hat{A}_F^\dagger,
\end{aligned} \quad (57)$$

where \hat{A}_F indicates an antilinear operator. Note the sign change of the imaginary number upon antilinear transformation. Now since

$$U_e(\tau_S, \tau_S - t)U_e(\tau_S - t, 0) = U_e(\tau_S, 0), \quad (58)$$

the equation above may be written as follows:

$$S' = \hat{O}_{\text{rev}} \hat{F} \cdot S: U'_e(t, 0) = \hat{A}_F U_e(\tau_S - t, 0)U_e(\tau_S, 0)^\dagger \hat{A}_F^\dagger. \quad (59)$$

The most useful relationship concerns the propagator over the complete sequence

$$U_e(\hat{O}_{\text{rev}} \hat{F} \cdot S) = \hat{A}_F U_e(S)^\dagger \hat{A}_F^\dagger. \quad (60)$$

This shows that the order reversal and antilinear transformation combine to give the *inverse* of the propagator, subjected to the same antilinear transformation.

Consider, for example, the effect of order reversal and phase inversion, for which $\hat{A}_F = R_y(\pi)\hat{K}$. The excitation propagators are related as follows:

$$U_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xz} \cdot S) = R_y(\pi)U_e(S)^\dagger R_y(\pi)^\dagger. \quad (61)$$

The Euler rotations are therefore transformed as follows:

$$\begin{aligned}
S' &= \hat{O}_{\text{rev}} \hat{\sigma}_{xz} \cdot S: \\
R_z(\alpha_e(S'))R_y(\beta_e(S'))R_z(\gamma_e(S')) \\
&= R_y(\pi)\{R_z(\alpha_e(S))R_y(\beta_e(S))R_z(\gamma_e(S))\}^\dagger R_y(\pi)^\dagger \\
&= R_y(\pi)R_z(-\gamma_e(S))R_y(-\beta_e(S))R_z(-\alpha_e(S))R_y(\pi)^\dagger \\
&= R_z(\gamma_e(S))R_y(-\beta_e(S))R_z(\alpha_e(S)),
\end{aligned} \quad (62)$$

leading to the correspondence

$$\begin{aligned}
\alpha_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xz} \cdot S) &= \gamma_e(S), \\
\beta_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xz} \cdot S) &= -\beta_e(S), \\
\gamma_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xz} \cdot S) &= \alpha_e(S).
\end{aligned} \quad (63)$$

Similarly, the combination of order reversal and frequency inversion, for which $\hat{A}_F = R_z(\pi)\hat{K}$, leads to the following relationship:

$$U_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xy} \cdot S) = R_z(\pi)U_e(S)^\dagger R_z(\pi)^\dagger. \quad (64)$$

In this case, the Euler angle correspondence is as follows:

$$\begin{aligned}
\alpha_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xy} \cdot S) &= -\gamma_e(S), \\
\beta_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xy} \cdot S) &= \beta_e(S),
\end{aligned} \quad (65)$$

$$\gamma_e(\hat{O}_{\text{rev}} \hat{\sigma}_{xy} \cdot S) = -\alpha_e(S).$$

3. Cyclic permutations

The complete excitation propagator transforms in a straightforward way under cyclic permutation of a pulse-sequence element. The relevant relationships are as follows:

$$\begin{aligned}
U_e(\hat{P}^+(\mathcal{E}) \cdot S) &= U_e(\mathcal{E})U_e(S)U_e(\mathcal{E})^\dagger, \\
U_e(\hat{P}^-(\mathcal{E}) \cdot S) &= U_e(\mathcal{E})^\dagger U_e(S)U_e(\mathcal{E}).
\end{aligned} \quad (66)$$

Cyclic permutation of an element \mathcal{E} subjects the overall sequence propagator to a unitary transformation under the propagator for \mathcal{E} .

IV. PULSE-SEQUENCE ELEMENTS

A. Basic elements

Symmetrical pulse sequences are constructed from individual building blocks. In general the building block of a pulse sequence is not a single pulse, but a sequence of pulses called the *basic element*, denoted here \mathcal{E} . The basic element may be any sequence of modulated excitation fields, and spans the interval τ_E . To draw an analogy with one-dimensional decorative tiling, the duration of the basic element τ_E is analogous to the length of the tile L , while the excitation modulation parameters defining the basic element are analogous to the color scheme of an individual tile.

The following cases are often encountered.

1. C-elements

If the total basic element propagator is proportional to the unity operator (within a phase factor), the basic element is called a *cycle*, and is denoted by the symbol \mathcal{C} . The requisite condition on the propagator is

$$U_e(\mathcal{C}) = \pm 1. \quad (67)$$

The excitation Euler angles are given by $\beta_e(\mathcal{C}) = 2\pi K$ and $\alpha_e(\mathcal{C}) + \gamma_e(\mathcal{C}) = 2\pi K'$ where K and K' are both integers.

If only the excitation field is taken into account, \mathcal{C} -elements leave spin states unchanged (within a phase factor). Some simple examples of \mathcal{C} -elements are 360_0 , $270_0 270_{180}$, and $90_0 360_{180} 270_0$.

2. R-elements

The basic element is referred to as a \mathcal{R} -element if the complete excitation propagator has the following form:

$$U_e(\mathcal{R}) = \pm R_z(\phi_R)R_x(\pi)R_z(-\phi_R), \quad (68)$$

where ϕ_R is called the effective phase of the \mathcal{R} -element, and may have any value. Sequences of this type invert the sign of longitudinal magnetization as follows:

$$U_e(\mathcal{R})I_z U_e(\mathcal{R})^\dagger = -I_z. \quad (69)$$

The excitation Euler angles for a \mathcal{R} -element are as follows:

$$\begin{aligned}
\alpha_e(\mathcal{R}) &= \phi_{\mathcal{R}} - \pi/2, \\
\beta_e(\mathcal{R}) &= (2K + 1)\pi, \\
\gamma_e(\mathcal{R}) &= -\phi_{\mathcal{R}} + \pi/2,
\end{aligned} \tag{70}$$

where K is an integer. Some simple examples of \mathcal{R} -elements are 180_0 , $90_0 270_{180}$, $90_{90} 180_0 90_{90}$, and $90_{90} 90_0 90_{90}$.

3. \mathcal{R}_0 -elements

A special case of an \mathcal{R} -element is an element that has an effective phase $\phi_{\mathcal{R}} = 0$. This is called a *zero-phase \mathcal{R} -element*, and is denoted here \mathcal{R}_0 . An element of this kind transforms the three components of spin angular momentum as follows:

$$\begin{aligned}
U_e(\mathcal{R}_0)I_xU_e(\mathcal{R}_0)^\dagger &= +I_x, \\
U_e(\mathcal{R}_0)I_yU_e(\mathcal{R}_0)^\dagger &= -I_y, \\
U_e(\mathcal{R}_0)I_zU_e(\mathcal{R}_0)^\dagger &= -I_z.
\end{aligned} \tag{71}$$

A \mathcal{R}_0 -element rotates the nuclei by an odd multiple of π around the rotating-frame x -axis.

The excitation Euler angles for a \mathcal{R}_0 -element are as follows:

$$\begin{aligned}
\alpha_e(\mathcal{R}_0) &= -\pi/2, \\
\beta_e(\mathcal{R}_0) &= (2K + 1)\pi, \\
\gamma_e(\mathcal{R}_0) &= +\pi/2,
\end{aligned} \tag{72}$$

where K is an integer.

The elements 180_0 and $90_0 270_{180}$ are \mathcal{R}_0 -elements since they only involve rotations about the x -axis. The sequence $90_{90} 180_0 90_{90}$ is also an \mathcal{R}_0 -element, since it fulfills all the conditions in Eq. (71). The sequence $90_{90} 90_0 90_{90}$, on the other hand, is not an \mathcal{R}_0 -element, since it has an effective phase $\phi_{\mathcal{R}} = \pi/4$. This may be seen from the following transformation properties:

$$\begin{aligned}
U_e(90_{90} 90_0 90_{90})I_xU_e(90_{90} 90_0 90_{90})^\dagger &= +I_y, \\
U_e(90_{90} 90_0 90_{90})I_yU_e(90_{90} 90_0 90_{90})^\dagger &= +I_x, \\
U_e(90_{90} 90_0 90_{90})I_zU_e(90_{90} 90_0 90_{90})^\dagger &= -I_z.
\end{aligned} \tag{73}$$

4. \mathcal{P} -elements

If the Euler angle β_e is equal to an odd multiple of $\pi/2$ when evaluated over the complete element, the basic element is denoted \mathcal{P} . The requisite condition is

$$\beta_e(\mathcal{P}) = (2K + 1)\pi/2, \tag{74}$$

where K is an integer. The angles $\alpha_e(\mathcal{P})$ and $\gamma_e(\mathcal{P})$ may have arbitrary values.

\mathcal{P} -elements convert angular momentum along the field into angular momentum perpendicular to the field. The phase of the transverse angular momentum is not constrained.

5. \mathcal{Z} -elements

\mathcal{Z} -elements induce a rotation around the rotating-frame z -axis, through an angle denoted $\phi_{\mathcal{Z}}$ as follows:

$$U_e(\mathcal{Z}) = R_z(\phi_{\mathcal{Z}}). \tag{75}$$

The Euler angles characterizing a \mathcal{Z} -element are given by

$$\begin{aligned}
\alpha_e(\mathcal{Z}) + \gamma_e(\mathcal{Z}) &= \phi_{\mathcal{Z}}, \\
\beta_e(\mathcal{Z}) &= 2\pi K,
\end{aligned} \tag{76}$$

where K is an integer. An example of a \mathcal{Z} -element with rotation angle $\phi_{\mathcal{Z}} = \phi$ is the composite z -pulse $90_{180}\phi_{90}90_0$.^{81,82}

B. Element symmetry

Pulse-sequence elements often have internal symmetry, which constrains the form of the excitation propagators.

1. Palindromic symmetry

A palindrome is a word or phrase that reads the same forwards or backwards (by convention, ignoring spaces), for example, “I prefer pi.” Similarly, a palindromic rf field has reflection symmetry about its central time point, in the rotating reference frame.

The definition of palindromic pulse-sequence symmetry requires care. Since the rf is the time derivative of the rf phase, reversing the order of all rf phases leads to a sign change in the rf offset frequency. A palindromic pulse sequence should therefore have *opposite* frequency offsets when reflected about its midpoint. The symmetry condition for a palindromic element is therefore

$$\mathcal{E} = \hat{\mathcal{O}}_{\text{rev}} \hat{\sigma}_{xy} \mathcal{E}, \tag{77}$$

not the more obvious $\mathcal{E} = \hat{\mathcal{O}}_{\text{rev}} \mathcal{E}$.

Similarly, a palindromic pulse sequence involving modulations of the longitudinal field must employ modulated fields with *opposite* signs when reflected about the midpoint of the sequence.

Palindromic elements include fixed-frequency composite pulses of the form $(\beta_1)_{\phi_1}(\beta_2)_{\phi_2}(\beta_1)_{\phi_1}$, as well as elements employing opposite frequency jumps, for example, $360_0^+ 360_0^-$, and frequency sweeps passing symmetrically through the center position.

From Eqs. (45) and (60), the excitation propagator of a palindromic element satisfies the following identity:

$$\mathcal{E} = \hat{\mathcal{O}}_{\text{rev}} \hat{\sigma}_{xy} \cdot \mathcal{E}: \quad U_e(\mathcal{E}) = R_z(\pi) U_e(\mathcal{E})^\dagger R_z(\pi)^\dagger. \tag{78}$$

This implies that the overall rotation generated by a palindromic element is always around an axis in the xy -plane. The same result may be expressed as follows in terms of the excitation Euler angles:

$$\mathcal{E} = \hat{\mathcal{O}}_{\text{rev}} \hat{\sigma}_{xy} \cdot \mathcal{E}: \quad \alpha_e(\mathcal{E}) = -\gamma_e(\mathcal{E}). \tag{79}$$

Many common pulse shapes used for frequency-selective excitation are palindromic. Examples include amplitude-shaped pulses of constant frequency⁸³ and symmetrical frequency sweeps.^{84,85}

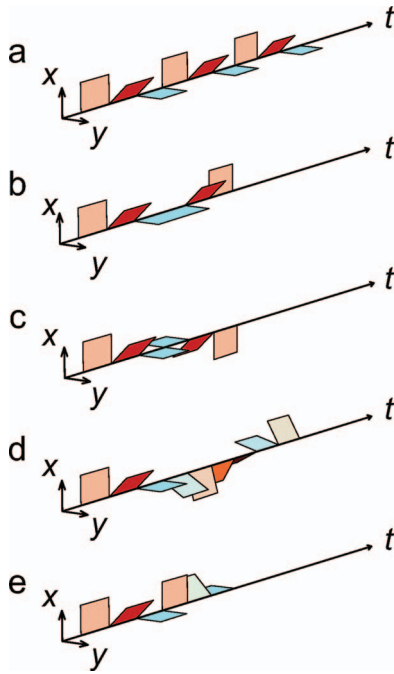


FIG. 3. (Color) The effect of five different pulse sequence expansions on the sequence $90_0 90_{45} 90_{90}$. (a) Repetition generated by $\hat{G}_{\text{rep}}(3)$; (b) palindromic expansion by $\hat{G}_{\text{pal}}(2)$; (c) antipalindromic expansion by $\hat{G}_{\text{antipal}}(2)$; (d) phase-step expansion generated by $\hat{G}_{\text{ph}}^1(3)$; mirror-pair expansion generated by $\hat{G}_{\sigma}(2)$.

2. Antipalindromic symmetry

The term *antipalindromic* is defined here to mean a pulse sequence which is invariant to reversing the order of the elements in time, changing the sign of all offset frequencies or z -modulation fields, and shifting all phases by an odd multiple of π . The relevant symmetry of the excitation fields is as follows:

$$\mathcal{E} = \hat{O}_{\text{rev}} \hat{\sigma}_{xy} \hat{\Phi}(K_{\text{odd}} \pi) \mathcal{E}, \quad (80)$$

where K is an odd integer. From Eq. (45) and (60), the excitation propagator of an antipalindromic element satisfies the following identity:

$$\mathcal{E} = \hat{O}_{\text{rev}} \hat{\Phi}(K_{\text{odd}} \pi) \hat{\sigma}_{xy} \cdot \mathcal{E}; \quad U_e(\mathcal{E}) = U_e(\mathcal{E})^\dagger. \quad (81)$$

This implies that the element propagator must be proportional to the unity operator, and hence that an antipalindromic element is a cycle ($\mathcal{E} = \mathcal{C}$).

Many pulse sequences employed in solid-state NMR are antipalindromic. Examples are the windowless WAHUHA cycle $90_0 90_{90} 90_{180} 90_{180}$ (Ref. 6) and the frequency-switched Lee–Goldburg sequence $360_0^+ 360_{180}^-$.^{62,63}

V. SYMMETRICAL EXPANSION

A. Generators

Suppose that a set of P modifiers is applied to the same pulse-sequence element \mathcal{E} , and the results chained together. The result is a pulse sequence \mathcal{S} that is P times longer than the starting sequence. This is called an expansion of order P , and may be written as

$$\mathcal{S} = \hat{G}(P) * \mathcal{E}, \quad (82)$$

where $\hat{G}(P)$ is an ordered list of P modifiers, called the *generator* of the expansion. An example is as follows:

$$\hat{G}(4) * 90_{90} 180_0 = 90_{90} 180_0 90_{180} 180_{90} 90_{-90} 180_0 180_0 90_{90}, \quad (83)$$

where the generator is

$$\hat{G}(4) = \{\hat{E}, \hat{\Phi}(\pi/2), \hat{\sigma}_{xz}, \hat{O}_{\text{rev}}\}. \quad (84)$$

Expansions may be nested. An expansion of order P_1 , followed by an expansion of order P_2 , is notated as

$$\mathcal{S} = \hat{G}_2(P_2) * \hat{G}_1(P_1) * \mathcal{E}. \quad (85)$$

Here the sequence \mathcal{S} is $P_1 P_2$ times longer than the element \mathcal{E} . An example is as follows:

$$\{\hat{E}, \hat{\Phi}(\pi)\} * \{\hat{E}, \hat{\Phi}(\pi)\} * 180_0 = 180_0 360_{180} 180_0. \quad (86)$$

B. Common expansions

Some common pulse-sequence expansions are examined below.

1. Repetition

The simplest expansion consists of repetition without change. The repetition of an element P times without change is denoted as

$$\hat{G}_{\text{rep}}(P) = \underbrace{\{\hat{E}, \dots, \hat{E}\}}_{P \text{ times}}. \quad (87)$$

A simple example is as follows:

$$90_{90} 180_0 90_{90} 180_0 = \hat{G}_{\text{rep}}(2) * 90_{90} 180_0. \quad (88)$$

The result of applying $\hat{G}_{\text{rep}}(3)$ to the sequence $90_0 90_{45} 90_{90}$ is illustrated in Fig. 3(a).

The effect of repeating a pulse sequence depends on the sequence type. Repetition of a cycle leads to another cycle. P -fold repetition of a \mathcal{Z} -element with rotation angle $\phi_{\mathcal{Z}}$ leads to another \mathcal{Z} -element with rotation angle $P\phi_{\mathcal{Z}}$. Twofold repetition of a \mathcal{R} -element, on the other hand, generates a cycle, since

$$\begin{aligned} U_e(\hat{G}_{\text{rep}}(2) * \mathcal{R}) &= U_e(\mathcal{R}\mathcal{R}) \\ &= R_z(\phi_{\mathcal{R}}) R_x(\pi) R_z(-\phi_{\mathcal{R}}) \cdot R_z(\phi_{\mathcal{R}}) R_x(\pi) R_z(-\phi_{\mathcal{R}}) \\ &= R_x(2\pi). \end{aligned} \quad (89)$$

2. Palindromic expansion

A twofold *palindromic expansion* of a pulse sequence is denoted as

$$\mathcal{S}' = \hat{G}_{\text{pal}}(2) * \mathcal{S}, \quad (90)$$

where the expansion generator is given by

$$\hat{\mathbf{G}}_{\text{pal}}(2) = \{\hat{E}, \hat{\sigma}_{xy} \hat{\sigma}_{\text{rev}}\}. \quad (91)$$

Examples of this equation are

$$90_{90}180_{90}90_{90} = \hat{\mathbf{G}}_{\text{pal}}(2) * 90_{90}90_{90}, \quad (92)$$

$$360_0^+ 360_0^- = \hat{\mathbf{G}}_{\text{pal}}(2) * 360_0^+.$$

The pulse sequence is written in reverse order and appended to itself, with a sign change in frequency offset (if applicable).

The result of applying $\hat{\mathbf{G}}_{\text{pal}}(2)$ to the sequence $90_{90}90_{45}90_{90}$ is illustrated in Fig. 3(b).

The following identities use Eq. (78) to show that palindromic expansion generates a cycle when applied to \mathcal{C} , \mathcal{R} , and \mathcal{Z} -elements:

$$\begin{aligned} U_e(\hat{\mathbf{G}}_{\text{pal}}(2) * \mathcal{C}) &= R_z(\pi) U_e(\mathcal{C})^\dagger R_z(\pi)^\dagger \cdot U_e(\mathcal{C}) = 1, \\ U_e(\hat{\mathbf{G}}_{\text{pal}}(2) * \mathcal{R}) &= R_z(\pi) U_e(\mathcal{R})^\dagger R_z(\pi)^\dagger \cdot U_e(\mathcal{R}) = R_z(2\pi), \\ U_e(\hat{\mathbf{G}}_{\text{pal}}(2) * \mathcal{Z}) &= R_z(\pi) U_e(\mathcal{Z})^\dagger R_z(\pi)^\dagger \cdot U_e(\mathcal{Z}) = 1. \end{aligned} \quad (93)$$

3. Antipalindromic expansion

A twofold *antipalindromic expansion* is denoted as

$$\mathcal{S}' = \hat{\mathbf{G}}_{\text{antipal}}(2) * \mathcal{S}, \quad (94)$$

where the generator is

$$\hat{\mathbf{G}}_{\text{antipal}}(2) = \{\hat{E}, \hat{\Phi}(\pi) \hat{\sigma}_{xy} \hat{\sigma}_{\text{rev}}\}. \quad (95)$$

Two examples are

$$90_{90}90_{90}90_{180}90_{270} = \hat{\mathbf{G}}_{\text{antipal}}(2) * 90_{90}90_{90}, \quad (96)$$

$$360_0^+ 360_{180}^- = \hat{\mathbf{G}}_{\text{antipal}}(2) * 360_0^+.$$

The last example is the frequency-switched Lee–Goldburg cycle.^{62,63} The result of applying $\hat{\mathbf{G}}_{\text{antipal}}(2)$ to the sequence $90_{90}90_{45}90_{90}$ is illustrated in Fig. 3(c).

Antipalindromic expansion of any element always generates a cycle, i.e., $\mathcal{C} = \hat{\mathbf{G}}_{\text{antipal}}(2) * \mathcal{E}$.

In the solid-state NMR literature, the antipalindromic expansion of a pulse sequence is often called “symmetrization.”^{7,13}

4. Phase-step expansion

A *phase-step expansion* of order P and winding number ν is denoted as

$$\mathcal{S}' = \hat{\mathbf{G}}_{\Phi}^{\nu}(P) * \mathcal{S}, \quad (97)$$

where the generator is

$$\hat{\mathbf{G}}_{\Phi}^{\nu}(P) = \{\hat{\Phi}(0), \hat{\Phi}(\Delta\phi), \hat{\Phi}(2\Delta\phi) \cdots \hat{\Phi}((P-1)\Delta\phi)\} \quad (98)$$

and the phase increment is defined

$$\Delta\phi = \pi\nu/P. \quad (99)$$

A phase-step expansion of order P and winding number ν generates a set of P equal phase shifts spanning ν complete rotations.

An example of a phase-step expansion is as follows:

$$\hat{\mathbf{G}}_{\Phi}^2(5) * 360_0 = 360_0 360_{144} 360_{288} 360_{432} 360_{576}. \quad (100)$$

A special case of a phase-step expansion involves just two phases, 0 and π . This is notated as follows for the sake of simplicity:

$$\hat{\mathbf{G}}_{\pi}(2) = \hat{\mathbf{G}}_{\Phi}^1(2) = \{\hat{E}, \hat{\Phi}(\pi)\}. \quad (101)$$

One example is as follows:

$$\hat{\mathbf{G}}_{\pi}(2) * 90_{90}90_{90} = 90_{90}90_{90}90_{270}90_{180}. \quad (102)$$

The result of applying $\hat{\mathbf{G}}_{\Phi}^1(3)$ to the sequence $90_{90}90_{45}90_{90}$ is illustrated in Fig. 3(d).

Phase-step cycles are frequently used in multiple-quantum NMR experiments. For example, selective ($\pm P$)-quantum excitation techniques use sequences generated by applying $\hat{\mathbf{G}}_{\Phi}^1(P)$. Phase-step cycles are also involved in the CN_{ν}^{ν} class of rotor-synchronized pulse sequences.^{31–33,35,53,71,73,76,86} The popular POST-C7 sequence³² is generated as follows:

$$\text{POST-C7} = \hat{\mathbf{G}}_{\Phi}^1(7) * 90_{180} 360_{270} 90_{180}. \quad (103)$$

In fact, the basic element of POST-C7 is itself generated by a twofold phase-step expansion of a simple element, followed by a cyclic permutation, so the full construction procedure is as follows:

$$\text{POST-C7} = \hat{\mathbf{G}}_{\Phi}^1(7) * \hat{\mathbf{P}}^-(90_{180}) \cdot \hat{\mathbf{G}}_{\pi}(2) * 360_0. \quad (104)$$

Phase-step expansion of a cycle generates another cycle; P -fold phase-step expansion of a \mathcal{Z} -element with rotation angle $\phi_{\mathcal{Z}}$ generates another \mathcal{Z} -element with rotation angle $P\phi_{\mathcal{Z}}$.

5. Mirror-pair expansion

A twofold *mirror-pair expansion* is denoted as follows:

$$\mathcal{S} = \hat{\mathbf{G}}_{\sigma}(2) * \mathcal{E}, \quad (105)$$

where

$$\hat{\mathbf{G}}_{\sigma}(2) = \{\hat{E}, \hat{\sigma}_{xz} \hat{\sigma}_{xy}\}. \quad (106)$$

The element is repeated once, changing the sign of all phases and offset frequencies. An example is as follows:

$$90_{90}90_{90}90_{-90}90_0 = \hat{\mathbf{G}}_{\sigma}(2) * (90_{90}90_0). \quad (107)$$

The result of applying $\hat{\mathbf{G}}_{\sigma}(2)$ to the sequence $90_{90}90_{45}90_{90}$ is illustrated in Fig. 3(e).

The following results use Eq. (56) to treat mirror-pair expansion applied to \mathcal{C} -, \mathcal{R} -, and \mathcal{Z} -elements:

$$U_e(\hat{\mathbf{G}}_\sigma(2)*\mathcal{C}) = R_x(-\pi)U_e(\mathcal{C})R_x(\pi) \cdot U_e(\mathcal{C}) = 1,$$

$$\begin{aligned} U_e(\hat{\mathbf{G}}_\sigma(2)*\mathcal{R}) &= R_x(-\pi)U_e(\mathcal{R})R_x(\pi) \cdot U_e(\mathcal{R}) \\ &= R_x(-\pi)R_z(\phi_{\mathcal{R}})R_x(\pi) \\ &\quad \times R_z(-\phi_{\mathcal{R}})R_x(\pi)R_z(\phi_{\mathcal{R}})R_x(\pi)R_z(-\phi_{\mathcal{R}}) \\ &= R_z(-4\phi_{\mathcal{R}})R_x(2\pi), \end{aligned} \quad (108)$$

$$U_e(\hat{\mathbf{G}}_\sigma(2)*\mathcal{Z}) = R_x(-\pi)U_e(\mathcal{Z})R_x(\pi) \cdot U_e(\mathcal{Z}) = 1.$$

This shows that mirror-pair expansion of \mathcal{C} and \mathcal{Z} -elements converts these elements into cycles, while mirror-pair expansion of a \mathcal{R} -element generates a \mathcal{Z} -element with rotation angle $\phi_{\mathcal{Z}} = -4\phi_{\mathcal{R}}$.

Mirror-pair expansion is employed in the construction of the RN_n^ν class of recoupling sequences.^{36–38,41,46,66,72,76} For example, the standard version of the $R20_2^9$ recoupling sequence⁴¹ is constructed as follows:

$$R20_2^9 = \hat{\mathbf{G}}_{\text{rep}}(10)*\hat{\mathbf{G}}_\sigma(2)*\hat{\Phi}(9\pi/20) \cdot 270_0 90_{180}. \quad (109)$$

C. Excitation Hamiltonian symmetry

Symmetrical expansion of a pulse-sequence element generates an excitation Hamiltonian obeying a defined symmetry relationship. An expansion of order P is associated with a set of superoperators \hat{H}_p and temporal operators \hat{T}_p , with $p \in \{0, 1, \dots, P-1\}$. The superoperators \hat{H}_p and temporal operators \hat{T}_p define the relationship between excitation Hamiltonians at symmetry-related time points, as follows:

$$\mathcal{H}_e(t_p) = \hat{H}_p \mathcal{H}_e(t_0), \quad (110)$$

where

$$t_p = \hat{T}_p t_0. \quad (111)$$

Note the relationship between Eqs. (110) and (111) for symmetrical excitation Hamiltonians and Eqs. (1) and (4) for decorative tiling.

The superoperator \hat{H}_p acts on an arbitrary operator Q as follows:

$$\hat{H}_p Q = H_p Q H_p^\dagger. \quad (112)$$

Depending on the pulse sequence symmetry the temporal operator \hat{T}_p may include a time-reversal operator \hat{T}_{rev} [see Eq. (49)] as well as a time-translation operator $\hat{\tau}_p$ as follows:

$$\hat{\tau}_p t = t + p\tau_E. \quad (113)$$

The operator $\hat{\tau}_p$ is the temporal equivalent of the spatial translation operator \hat{X}_p [see Eq. (2)].

The superoperator \hat{H}_p is periodic,

$$\hat{H}_{p+KP} = \hat{H}_p, \quad (114)$$

while the temporal operator has time-translation symmetry

$$\hat{T}_{p+KP} = \hat{\tau}_p^K \hat{T}_p. \quad (115)$$

The operator sets for the common symmetry expansions are as follows

(1) Repetition:

$$\hat{\mathbf{G}}_{\text{rep}}(P): H_p = \hat{1}, \quad \hat{T}_p = \hat{\tau}_p. \quad (116)$$

(2) Phase-step expansion of order P and winding number ν :

$$\hat{\mathbf{G}}_\Phi^\nu(P): H_p = R_z(2\pi p\nu/P), \quad \hat{T}_p = \hat{\tau}_p. \quad (117)$$

(3) Mirror-pair expansion:

$$\hat{\mathbf{G}}_\sigma(2): \begin{cases} H_0 = \hat{1}, & \hat{T}_0 = \hat{\tau}_0 \\ H_1 = R_x(-\pi), & \hat{T}_1 = \hat{\tau}_1. \end{cases}$$

(4) Palindromic expansion:

$$\hat{\mathbf{G}}_{\text{pal}}(2): \begin{cases} H_0 = \hat{1}, & \hat{T}_0 = \hat{\tau}_0 \\ H_1 = R_z(\pi)\hat{K}, & \hat{T}_1 = \hat{\tau}_1 \hat{T}_{\text{rev}}. \end{cases}$$

(5) Antipalindromic expansion:

$$\hat{\mathbf{G}}_{\text{antipal}}(2): \begin{cases} H_0 = \hat{1}, & \hat{T}_0 = \hat{\tau}_0 \\ H_1 = \hat{K}, & \hat{T}_1 = \hat{\tau}_1 \hat{T}_{\text{rev}}. \end{cases}$$

Note that the palindromic and antipalindromic expansions involve antilinear operators as well as time reversal.

D. Propagator symmetry

Symmetry expansion of a pulse sequence generates symmetry in the excitation Hamiltonian, which leads in turn to symmetry in the excitation propagator. The general symmetry relationship for the excitation propagator may be notated as follows:

$$U_e(\hat{T}_p t_0, 0) = \hat{U}_p U_e(t_0, 0). \quad (118)$$

The spin system propagators from $t=0$ up to all symmetry-related time points $\hat{T}_p t_0$ are related by application of the set of superoperators \hat{U}_p . In general, these symmetry superoperators have the following property:

$$\hat{U}_p Q = V_p Q W_p. \quad (119)$$

The symmetry superoperator \hat{U}_p multiplies its operand with an operator V_p from the left, and the operator W_p from the right. The operators \hat{T}_p , V_p , and W_p are characteristic of the symmetry expansion.

1. Linear transformations

If all temporal operators are time-translation operators $\hat{T}_p = \hat{\tau}_p$, and all Hamiltonian transformation operators H_p are linear, the left-side operator V_p is given as follows:

$$V_p = H_p, \quad (120)$$

while the right-side operator W_p is defined by the following recursion:

$$W_p = H_p^\dagger V_{p-1} U_e(\mathcal{E}) W_{p-1}, \quad (121)$$

with the seed

$$W_0 = V_0^\dagger. \quad (122)$$

Equation (121) shows that the symmetry operators for the propagator depend not only on the symmetry transformations themselves but also on the accumulated product of previous propagators, and hence the type of element to which the sequence is applied.

The range of possibilities is very large and I will only discuss a few cases whose importance has already been demonstrated.

- (1) *Symmetry expansion of a cycle.* The simplest case is when a symmetry expansion is applied to a cycle, since the propagator $U_e(\mathcal{E})$ is proportional to the unity operator. From Eqs. (121) and (122), the right-side symmetry operators W_p accumulate as follows:

$$\mathcal{E} = C: \quad W_0 = V_0^\dagger = H_0^\dagger,$$

$$W_1 = H_1^\dagger V_0 W_0 = H_1^\dagger V_0 V_0^\dagger = H_1^\dagger, \quad (123)$$

$$W_2 = H_2^\dagger V_1 W_1 = H_2^\dagger H_1 H_1^\dagger = H_2^\dagger,$$

and so on. In general, for symmetry expansion of a cycle, we get

$$W_p = H_p^\dagger \quad (124)$$

and hence

$$U_e(\hat{\tau}_p t_0, 0) = H_p U_e(t_0, 0) H_p^\dagger. \quad (125)$$

The modifications of the Hamiltonian are transferred directly to the propagators in this case.

As an example, consider a phase-step expansion with order P and winding number ν , applied to a cycle, as follows:

$$S = \hat{\mathbf{G}}_\Phi^\nu(P) * C. \quad (126)$$

The excitation Hamiltonians at corresponding time points are related by rotations around the z -axis as follows:

$$H_p = R_z\left(\frac{2\pi\nu p}{P}\right). \quad (127)$$

This relationship is transferred without modification to the symmetry-related propagators as follows:

$$U_e(t_p, 0) = R_z\left(\frac{2\pi\nu p}{P}\right) U_e(t_0, 0) R_z\left(\frac{2\pi\nu p}{P}\right)^\dagger. \quad (128)$$

The excitation Euler angles at corresponding time

points are therefore related as follows:

$$\hat{\mathbf{G}}_\Phi^\nu(P) * C: \begin{cases} \alpha_e(t_p) = \alpha_e(t_0) + 2\pi\nu p/P \\ \beta_e(t_p) = \beta_e(t_0) \\ \gamma_e(t_p) = \gamma_e(t_0) - 2\pi\nu p/P. \end{cases} \quad (129)$$

- (2) *Repetition of a \mathcal{Z} -element.* The excitation propagator for a \mathcal{Z} -element is defined by

$$U_e(\mathcal{Z}) = R_z(\phi_{\mathcal{Z}}), \quad (130)$$

where $\phi_{\mathcal{Z}}$ is the rotation angle of the element. If the \mathcal{Z} -element is repeated without change, all operators H_p are equal to unity, so the right-hand operators W_p in Eq. (121) are given by

$$\hat{\mathbf{G}}_{\text{rep}}(P) * \mathcal{Z}: \quad W_0 = V_0^\dagger = 1,$$

$$W_1 = H_1^\dagger V_0 U_e(\mathcal{E}) W_0 = R_z(\phi_{\mathcal{Z}}), \quad (131)$$

$$W_2 = H_2^\dagger V_1 U_e(\mathcal{E}) W_1 = R_z(2\phi_{\mathcal{Z}}).$$

The excitation propagators at corresponding time points are therefore related as follows:

$$U_e(t_p, 0) = U_e(t_0, 0) R_z(p\phi_{\mathcal{Z}}) \quad (132)$$

and so on. The symmetry relationships between Euler angles at corresponding time points are given by

$$\hat{\mathbf{G}}_{\text{rep}}(P) * \mathcal{Z}: \begin{cases} \alpha_e(t_p) = \alpha_e(t_0) \\ \beta_e(t_p) = \beta_e(t_0) \\ \gamma_e(t_p) = \gamma_e(t_0) + p\phi_{\mathcal{Z}}. \end{cases} \quad (133)$$

Comparison with Eq. (129) shows that the effect on the β_e and γ_e Euler angles is similar to that generated by phase-stepping a cycle. The α_e Euler angle behaves differently, however.

- (3) *Repetition of a \mathcal{R} -element.* The rf propagator for a general \mathcal{R} -element is given by

$$U_e(\mathcal{R}) = R_z(\phi_{\mathcal{R}}) R_x(\pi) R_z(\phi_{\mathcal{R}})^\dagger = R_x(\pi) R_z(-2\phi_{\mathcal{R}}), \quad (134)$$

where $\phi_{\mathcal{R}}$ is the effective phase. The right-hand operators for duplication of a \mathcal{R} -element are therefore given by

$$W_0 = V_0^\dagger = H_0^\dagger = 1,$$

$$W_1 = H_1^\dagger V_0 U_e(\mathcal{R}) W_0 = R_x(\pi) R_z(-2\phi_{\mathcal{R}}), \quad (135)$$

$$\begin{aligned} W_2 &= H_2^\dagger V_1 U_e(\mathcal{R}) W_1 \\ &= R_x(\pi) R_z(-2\phi_{\mathcal{R}}) \cdot R_x(\pi) R_z(-2\phi_{\mathcal{R}}) = R_x(2\pi), \end{aligned}$$

or in general

$$W_p = \begin{cases} R_x(p\pi) & \text{for even } p \\ R_x(p\pi)R_z(-2\phi_R) & \text{for odd } p. \end{cases} \quad (136)$$

This leads to the following Euler angle relationships:

$$\hat{\mathbf{G}}_{\text{rep}}(P)*\mathcal{R}: \begin{cases} \alpha_e(t_p) = \alpha_e(t_0) \\ \beta_e(t_p) = p\pi + \beta_e(t_0) \\ \gamma_e(t_p) = \begin{cases} \gamma_e(t_0) & \text{for even } p \\ -\gamma_e(t_0) - 2\phi_R & \text{for odd } p. \end{cases} \end{cases} \quad (137)$$

- (4) *Mirror-pair expansion of a \mathcal{R} -element.* Mirror-pair expansion is defined by the operators

$$\hat{\mathbf{G}}_\sigma(2) = \{\hat{E}, \hat{\sigma}_{xz}\hat{\sigma}_{xy}\}, \quad (138)$$

for which the Hamiltonian transformation operators are

$$\{H_0, H_1\} = \{1, R_x(-\pi)\}, \quad (139)$$

which are both linear. If mirror-pair expansion is applied to a \mathcal{R} -element, the propagator symmetry operators are as follows

$$\begin{aligned} V_0 &= H_0 = 1, \\ W_0 &= V_0^\dagger = 1, \\ V_1 &= H_1 = R_x(-\pi), \\ W_1 &= H_1^\dagger V_0 U_e(\mathcal{R}) W_0 \\ &= R_x(\pi) R_x(\pi) R_z(-2\phi_R) \\ &= R_x(2\pi) R_x(-2\phi_R). \end{aligned} \quad (140)$$

This leads to the following symmetry relationship between propagators at corresponding time points:

$$U_e(t_1, 0) = R_x(\pi) U_e(t_0, 0) R_z(-2\phi_R) \quad (141)$$

and hence the following Euler angle relationships:

$$\hat{\mathbf{G}}_\sigma(2)*\mathcal{R}: \begin{cases} \alpha_e(t_1) = -\pi - \alpha_e(t_0) \\ \beta_e(t_1) = \pi + \beta_e(t_0) \\ \gamma_e(t_1) = \gamma_e(t_0) - 2\phi_R. \end{cases} \quad (142)$$

- (5) *Fourfold decoupling sequence expansion.* Heteronuclear decoupling sequences may be generated by repeating a \mathcal{R} -element and applying a two fold phase-step expansion to the result¹⁸

$$S = \hat{\mathbf{G}}_\pi(2)*\hat{\mathbf{G}}_{\text{rep}}(2)*\mathcal{R}. \quad (143)$$

The first stage in the expansion may be treated using Eq. (137). Since the product of two \mathcal{R} -elements is a cycle, the second stage may be treated using Eq. (129). The symmetries of the Euler angles may therefore be

summarized as follows:

p	α_e	β_e	γ_e
0	$\alpha_e(t_0)$	$\beta_e(t_0)$	$\gamma_e(t_0)$
1	$\alpha_e(t_0)$	$\pi + \beta_e(t_0)$	$\pi - \gamma_e(t_0) - 2\phi_R$
2	$\pi + \alpha_e(t_0)$	$\beta_e(t_0)$	$-\pi + \gamma_e(t_0)$
3	$\pi + \alpha_e(t_0)$	$\pi + \beta_e(t_0)$	$-\gamma_e(t_0) - 2\phi_R$

The implications of this relationship are discussed below.

- (6) RN_n^ν *recoupling sequences.* Recoupling sequences in the class RN_n^ν are generated as follows:

$$RN_n^\nu = \hat{\mathbf{G}}_{\text{rep}}\left(\frac{N}{2}\right)*\hat{\mathbf{G}}_\sigma(2)*\mathcal{R}, \quad (144)$$

where N is an even integer, and the \mathcal{R} -element is itself generated by phase-shifting a \mathcal{R}_0 -element as follows:

$$\mathcal{R} = \hat{\Phi}\left(\frac{\pi\nu}{N}\right) \cdot \mathcal{R}_0. \quad (145)$$

This ensures that the \mathcal{R} -element has an effective phase angle $\phi_R = \pi\nu/N$. The mirror-pair expansion $\hat{\mathbf{G}}_\sigma(2)$ imposes the Euler angle relationships in Eq. (142). The repetition $\hat{\mathbf{G}}_{\text{rep}}$ imposes the Euler angle relationships in Eq. (133), since the mirror-pair of \mathcal{R} -elements is equal to a \mathcal{Z} -element with rotation angle $\phi_Z = -4\phi_R$ [see Eq. (108)]. The Euler angle symmetries for the expansion in Eqs. (144) and (145) are therefore

$$\left. \begin{aligned} \alpha_e(t_p) &= \alpha_e(t_0) \\ \beta_e(t_p) &= \beta_e(t_0) \\ \gamma_e(t_p) &= \gamma_e(t_0) - 2\pi p\nu/N \end{aligned} \right\} \text{ for even } p, \quad (146)$$

$$\left. \begin{aligned} \alpha_e(t_p) &= -\pi - \alpha_e(t_0) \\ \beta_e(t_p) &= \pi + \beta_e(t_0) \\ \gamma_e(t_p) &= \gamma_e(t_0) - 2\pi p\nu/N \end{aligned} \right\} \text{ for odd } p,$$

where $p \in \{0, 1, \dots, N-1\}$. This result may be compared to that for CN_n^ν sequences, given in Eq. (129). The symmetry of the γ_e Euler angle is the same in the two cases. The behavior of the β_e Euler angle is also similar, except for the addition of π on odd values of p in the RN_n^ν case.

2. Twofold antilinear expansions

Expansions involving antilinear transformation operators are usually accompanied by time reversal, as described in Eq. (118). For these twofold expansions, the relevant relationship between the propagators may be derived by repeating the arguments in Eq. (57). This leads to propagator relationships of the form

$$U_e(t_0, 0) = \hat{A}_F U_e(2\tau_E, t_1)^\dagger \hat{A}_F^\dagger = \hat{A}_F U_e(t_1, 0) U_e(2\tau_E, 0)^\dagger \hat{A}_F^\dagger, \quad (147)$$

where \hat{A}_F indicates the relevant antilinear transformation operator, and the symmetry-related time points have the relationship

$$t_1 = \hat{\tau}_1 \hat{T}_{\text{rev}} t_0 = 2\tau_E - t_0. \quad (148)$$

In the special case of antipalindromic expansion, the propagator over the complete sequence is proportional to the unity operator, and the antilinear transformation operator is given by the time-reversal operator \hat{K} [see Eq. (118)]. In this case, Eq. (147) becomes

$$\hat{G}_{\text{antipal}}(2) \cdot \mathcal{E}: U_e(t_0, 0) = \hat{K} U_e(t_1, 0) \hat{K}^\dagger. \quad (149)$$

The time-reversal operator \hat{K} commutes with any rotation operator, since, for example,

$$\begin{aligned} \hat{K} \exp\{-i\theta I_\mu\} \hat{K}^\dagger &= \exp\{+i\theta \hat{K} I_\mu \hat{K}^\dagger\} \\ &= \exp\{+i\theta(-I_\mu)\} \\ &= \exp\{-i\theta I_\mu\}. \end{aligned} \quad (150)$$

As a result, antipalindromic expansion of an element leads to *palindromic* symmetry for the propagator under the excitation field

$$\hat{G}_{\text{antipal}}(2) \cdot \mathcal{E}: U_e(t_0, 0) = U_e(t_1, 0). \quad (151)$$

This corresponds to the following Euler angle relationships:

$$\hat{G}_{\text{antipal}}(2) \cdot \mathcal{E}: \begin{cases} \alpha_e(t_1) = \alpha_e(t_0) \\ \beta_e(t_1) = \beta_e(t_0) \\ \gamma_e(t_1) = \gamma_e(t_0). \end{cases} \quad (152)$$

VI. AVERAGE HAMILTONIAN THEORY

The average Hamiltonian theory of Mansfield⁷ and Haeberlen and Waugh⁶ is of central importance in NMR pulse-sequence design. It is now reviewed briefly in order to establish the notation and to emphasize some salient points.

Average Hamiltonian theory is usually applied in the context of a relatively small internal Hamiltonian $\mathcal{H}_i(t)$, representing the interactions of the nuclei with their immediate molecular environment, and an external Hamiltonian $\mathcal{H}_e(t)$ which represents the interactions of the nuclei with the excitation field (consisting of the rf field, plus modulated longitudinal fields, in general) as follows.

$$\mathcal{H}(t) = \mathcal{H}_i(t) + \mathcal{H}_e(t). \quad (153)$$

The two terms do not commute in general. The propagator for the spin system from time point t_a up to a general time t solves the equation

$$\frac{d}{dt} U(t, t_a) = -i\mathcal{H}(t) U(t, t_a), \quad (154)$$

with the initial condition $U(t_a, t_a) = 1$. An exact solution for $U(t, t_a)$ is difficult to find in many cases.

The problem is often treated by defining an interaction-frame internal Hamiltonian $\tilde{\mathcal{H}}_i(t)$ through

$$\tilde{\mathcal{H}}_i(t) = U_e(0, t) \mathcal{H}_i(t) U_e(t, 0), \quad (155)$$

where U_e is the propagator under the excitation fields [Eq. (25)], and $t=0$ is the time point at which the interaction frame coincides with the ordinary rotating frame. The propagator between time points t_a and t_b is given by

$$U(t_b, t_a) = U_e(0, t_b) \tilde{U}_i(t_b, t_a) U_e(t_a, 0), \quad (156)$$

where the interaction-frame propagator solves

$$\frac{d}{dt} \tilde{U}_i(t, t_a) = -i\tilde{\mathcal{H}}_i(t) \tilde{U}_i(t, t_a). \quad (157)$$

If \mathcal{H}_i is assumed to be smaller than \mathcal{H}_e , an approximate solution for Eq. (157) is often easier to find than for Eq. (154).

In general, the interaction-frame propagator $\tilde{U}_i(t_b, t_a)$ may always be written as

$$\tilde{U}_i(t_b, t_a) = \exp\{-i\bar{\mathcal{H}}_i(t_b, t_a) \tau_{ba}\}, \quad (158)$$

where $\bar{\mathcal{H}}_i$ is the *effective Hamiltonian* over the time interval of duration $\tau_{ba} = t_b - t_a$. In the formulation of average Hamiltonian theory using the Magnus expansion, this effective Hamiltonian is written using a series expansion in powers of the Hamiltonian multiplied by the time interval, i.e.,

$$\bar{\mathcal{H}}_i(t_b, t_a) = \bar{\mathcal{H}}_i^{(1)}(t_b, t_a) + \bar{\mathcal{H}}_i^{(2)}(t_b, t_a) + \cdots, \quad (159)$$

where the first two terms are as follows:^{6,7,13}

$$\begin{aligned} \bar{\mathcal{H}}_i^{(1)}(t_b, t_a) &= \tau_{ba}^{-1} \int_{t_a}^{t_b} dt \tilde{\mathcal{H}}_i(t), \\ \bar{\mathcal{H}}_i^{(2)}(t_b, t_a) &= (2i\tau_{ba})^{-1} \int_{t_a}^{t_b} dt_2 \int_{t_a}^{t_2} dt_1 [\tilde{\mathcal{H}}_i(t_2), \tilde{\mathcal{H}}_i(t_1)]. \end{aligned} \quad (160)$$

The superscript numbering scheme used in the early AHT literature differs from this by 1 (the first term having an index of 0). The numbering scheme used here and in many recent papers is more intuitive since the superscript directly indicates the power of the spin Hamiltonian.

The term $\bar{\mathcal{H}}_i^{(1)}(t_b, t_a)$ is equal to the *average Hamiltonian* over the interval τ_{ba} . The terms $\bar{\mathcal{H}}_i^{(n)}(t_b, t_a)$ with $n \geq 2$ are usually interpreted as correction terms to the average Hamiltonian.

If the interaction-frame Hamiltonian is periodic, with period τ_S , all average Hamiltonian terms are the same when evaluated over any number of complete periods as follows:

$$\bar{\mathcal{H}}_i^{(n)}(\hat{G}_{\text{rep}}(P) * C) = \bar{\mathcal{H}}_i^{(n)}(C). \quad (161)$$

However, in general, the average Hamiltonian theory may also be applied to incomplete periods of a periodic system, and to problems that lack periodicity.

TABLE I. Rotational signatures of homonuclear spin interactions in diamagnetic materials.

Interaction	Space rank ℓ	Spin rank λ	Field rank Y
Isotropic chemical shift	0	1	1
Antisymmetric part of chemical shift tensor	1	1	1
Chemical shift anisotropy	2	1	1
Isotropic J-coupling	0	0	0
Antisymmetric part of J-coupling tensor	1	1	0
J-coupling anisotropy	2	2	0
Direct dipole-dipole coupling	2	2	0
Electric quadrupole coupling	2	2	0

VII. INTERNAL HAMILTONIANS

The internal spin Hamiltonian \mathcal{H}_i contains a set of terms, each one representing a different physical influence on the nuclear spin Hamiltonian, i.e., chemical shift, direct dipole-dipole coupling, indirect dipole-dipole coupling, electric quadrupole coupling, and so on.

A. Rotational signatures

Each interaction term is conveniently classified in terms of its transformation properties under various types of rotation. The terms are conveniently represented as irreducible spherical tensors with a set of characteristic integer ranks, describing their rotational symmetry under a particular type of rotation. In systems of only one nuclear spin species, the relevant rotations are (i) rotations of the nuclear spin states; (ii) rotations of the nuclear coordinates—as effected physically by rotations of the molecules or mechanical rotations of the entire sample; and (iii) in the case of chemical shift terms, rotations of the external magnetic field, which participates in the nuclear spin interaction by inducing currents in the molecular electron clouds. If more than one nuclear species is present, individual rotational ranks may be specified for the different nuclear species.

The set of rotational ranks for a given spin interaction is called here the *rotational signature*.⁷⁶

Incidentally, the frequently encountered terms “spin space” and “real space” are misleading fallacies—the nuclear spins and the molecules rotate in the *same* three-dimensional space. One does not speak of a “rotation in shoe space” when a shoe is rotated, and the same considerations apply to a nuclear spin.

The most important spin interaction terms in homonuclear systems are summarized in Table I, which shows the rank λ for spatial rotations of the nuclear spin polarizations, the rank ℓ for spatial rotations of the nuclear coordinates, and a third rank, denoted here Y , for spatial rotations of the external magnetic field.⁷⁶

Since space is isotropic, all terms are rank-0 with respect to rotations of *everything* (i.e., the nuclear spins, the nuclear coordinates, and the magnetic field, all at the same time). The isotropy is broken when only one of the interacting objects is rotated, leaving the others unchanged. The rotational ranks in Table I refer to such isolated rotations.

Table I may be interpreted mathematically as follows: The internal spin Hamiltonian is expressed as a sum of terms representing different physical interactions as follows:

$$\mathcal{H}_i = \sum_{\Lambda} \mathcal{H}^{\Lambda}. \quad (162)$$

Each interaction may be expressed as a set of components which transform as irreducible spherical tensors of rank ℓ for rotations of the spatial coordinates, and rotations of rank λ for the spin polarizations as follows:

$$\mathcal{H}^{\Lambda} = \sum_{\ell, \lambda} \mathcal{H}_{\ell\lambda}^{\Lambda}. \quad (163)$$

For example, the chemical shift interaction consists of a component with $\{\ell, \lambda\} = \{0, 1\}$ (the isotropic chemical shift), a component with $\{\ell, \lambda\} = \{1, 1\}$ (the antisymmetric part of the chemical shift tensor—which is usually of marginal importance), and a component with $\{\ell, \lambda\} = \{2, 1\}$ (the chemical shift anisotropy).

The spin interaction term $\mathcal{H}_{\ell\lambda}^{\Lambda}$ itself consists of $(2\ell+1)(2\lambda+1)$ components with spatial quantum numbers $m \in \{-\ell, -\ell+1, \dots, \ell\}$ and spin quantum numbers $\mu \in \{-\lambda, -\lambda+1, \dots, \lambda\}$ as follows:

$$\mathcal{H}_{\ell\lambda}^{\Lambda} = \sum_{m=-\ell}^{+\ell} \sum_{\mu=-\lambda}^{+\lambda} \mathcal{H}_{\ell m \lambda \mu}^{\Lambda}. \quad (164)$$

The individual components $\mathcal{H}_{\ell m \lambda \mu}^{\Lambda}$ may be combined in two different ways, depending on the context of the problem.

1. Spin rotations

The components may be summed over the spatial quantum number m , so as to construct the components $\mathcal{H}_{\ell\lambda\mu}^{\Lambda}$ of an irreducible spherical tensor with rank λ for rotations of the spin polarizations,

$$\mathcal{H}_{\ell\lambda\mu}^{\Lambda} = \sum_{m=-\ell}^{+\ell} \mathcal{H}_{\ell m \lambda \mu}^{\Lambda}. \quad (165)$$

These components transform as follows under rotations of the nuclear spin states:

$$R(\Omega_{\text{spin}}) \mathcal{H}_{\ell\lambda\mu}^{\Lambda} R(\Omega_{\text{spin}})^{\dagger} = \sum_{\mu'=-\lambda}^{+\lambda} \mathcal{H}_{\ell\lambda\mu'}^{\Lambda} D_{\mu'\mu}^{\Lambda}(\Omega_{\text{spin}}), \quad (166)$$

where the rotation Euler angles are $\Omega_{\text{spin}} = \{\alpha, \beta, \lambda\}$, and a general element of the Wigner matrix of rank λ is given by

TABLE II. Rotational signatures of the most important interactions for heteronuclear spin systems in diamagnetic materials.

Interaction	Space rank ℓ	Spin rank λ_I	Spin rank λ_S	Field rank Y
I -spin isotropic shift	0	1	0	1
I -spin CSA	2	1	0	1
I -spin J-coupling	0	0	0	0
I -spin DD-coupling	2	2	0	0
S -spin isotropic shift	0	0	1	1
S -spin CSA	2	0	1	1
S -spin J-coupling	0	0	0	0
S -spin DD-coupling	2	0	2	0
IS J-coupling	0	1	1	0
IS DD-coupling	2	1	1	0

$$D_{\mu'\mu}^{\lambda}(\Omega_{\text{spin}}) = \exp\{-i\mu'\alpha\}d_{\mu'\mu}^{\lambda}(\beta)\exp\{-i\mu\gamma\} \quad (167)$$

and d is a reduced Wigner matrix element.

2. Spatial rotations

The components may be summed over the spin quantum number μ , so as to construct the components $\mathcal{H}_{\ell m \lambda}^{\Lambda}$ of an irreducible spherical tensor with rank ℓ for rotations of the spatial coordinates,

$$\mathcal{H}_{\ell m \lambda}^{\Lambda} = \sum_{\mu=-\lambda}^{+\lambda} \mathcal{H}_{\ell m \lambda \mu}^{\Lambda}. \quad (168)$$

These components transform under spatial rotations of the nuclear positions as follows:

$$R(\Omega_{\text{space}})\mathcal{H}_{\ell m \lambda}^{\Lambda}R(\Omega_{\text{space}})^{\dagger} = \sum_{m'=-\ell}^{+\ell} \mathcal{H}_{\ell m' \lambda}^{\Lambda}D_{m'm}^{\ell}(\Omega_{\text{space}}). \quad (169)$$

3. Heteronuclear interactions

A rotational rank table for the most important interaction terms in *heteronuclear* spin systems is shown in Table II. In this case, individual ranks λ_I and λ_S are introduced for individual rotations of the polarizations of the spin species I and S , respectively.

B. High-field Hamiltonians

In high magnetic field, the spin Hamiltonians are truncated by the secular approximation. This removes all interaction terms with $\mu \neq 0$ and $m \neq 0$. The high-field internal spin Hamiltonian is given by

$$\mathcal{H}_i \cong \sum_{\Lambda} \sum_{\ell, \lambda} \mathcal{H}_{\ell 0 \lambda 0}^{\Lambda} \quad (\text{in high field}). \quad (170)$$

C. Interaction frame

A high-field internal Hamiltonian term $\mathcal{H}_{\ell 0 \lambda 0}^{\Lambda}$ may be transformed into the interaction frame of the excitation field using Eq. (155). The rotation by the excitation field may be expressed in terms of Euler angles as follows:

$$U_e(t, 0) = R_z(\alpha_e(t))R_y(\beta_e(t))R_z(\gamma_e(t)) \quad (171)$$

and hence

$$U_e(0, t) = R_z(-\gamma_e(t))R_y(-\beta_e(t))R_z(-\alpha_e(t)). \quad (172)$$

The interaction-frame Hamiltonian may therefore be written as

$$\tilde{\mathcal{H}}_i(t) = \sum_{\Lambda, \ell, \lambda, \mu} \tilde{\mathcal{H}}_{\ell 0 \lambda \mu}^{\Lambda}(t), \quad (173)$$

where

$$\tilde{\mathcal{H}}_{\ell 0 \lambda \mu}^{\Lambda}(t) = \mathcal{H}_{\ell 0 \lambda \mu}^{\Lambda} \sigma_{\lambda \mu}(t) \quad (174)$$

and the following abbreviation is introduced:

$$\sigma_{\lambda \mu}(t) = \exp\{+i\mu\gamma_e(t)\}d_{\mu 0}^{\lambda}(-\beta_e(t)). \quad (175)$$

Note that the excitation Euler angle α_e is not involved.

VIII. SELECTION RULES

The symmetry of the pulse sequence interacts with the rotational symmetries of the spin interaction terms to generate *selection rules* for the symmetry-allowed average Hamiltonian terms.

A. Stationary samples

In a stationary sample, we may assume that the internal Hamiltonians $\mathcal{H}_{\ell \lambda 0}^{\Lambda}$ are time independent, after averaging over rapid molecular motion. In this case, the time dependence of the interaction-frame terms $\tilde{\mathcal{H}}_{\ell \lambda \mu}^{\Lambda}$ is due solely to the motion of the frame, and hence the influence of the excitation fields.

1. Symmetry expansions

Suppose that a pulse-sequence element \mathcal{E} is subjected to a symmetrical expansion of order P , i.e., $S = \hat{G}(P) \star \mathcal{E}$. The symmetrical expansion is defined by a set of P excitation field modifiers and P temporal modifiers as described above. This leads to a set of defined relationships between the excitation field Euler angles $\{\alpha_e(t_p), \beta_e(t_p), \gamma_e(t_p)\}$ at all time points t_p within the p th element, and the excitation field Euler angles at symmetry-related time points within the basic element, from which the expanded sequence is derived.

The first two average Hamiltonian terms may therefore be written as follows:

$$\bar{\mathcal{H}}_i^{(1)}(S) = \sum_{\Lambda, \ell, \lambda, \mu} \bar{\mathcal{H}}_{\ell 0 \lambda \mu}^{\Lambda(1)}(S), \quad (176)$$

$$\bar{\mathcal{H}}_i^{(2)}(S) = \sum_{\Lambda_2, \ell_2, \lambda_2, \mu_2, \Lambda_1, \ell_1, \lambda_1, \mu_1} \bar{\mathcal{H}}_{\ell_2 0 \lambda_2 \mu_2 \ell_1 0 \lambda_1 \mu_1}^{\Lambda_2 \Lambda_1(2)}(S),$$

where the first-order term is given by

$$\bar{\mathcal{H}}_{\ell 0 \lambda \mu}^{\Lambda(1)}(S) = \mathcal{H}_{\ell 0 \lambda \mu}^{\Lambda} \times \tau_E^{-1} \int_0^{\tau_E} dt \Sigma_{\lambda \mu}(t) \quad (177)$$

and

$$\Sigma_{\lambda \mu}(t) = P^{-1} \sum_{p=0}^{p-1} \sigma_{\lambda \mu}(\hat{T}_p t). \quad (178)$$

Here $\sigma_{\lambda \mu}$ is defined in Eq. (175). Similarly, the second-order term is given by

$$\begin{aligned} \bar{\mathcal{H}}_{\ell_2 0 \lambda_2 \mu_2 \ell_1 0 \lambda_1 \mu_1}^{\Lambda_2 \Lambda_1(2)}(S) \\ = [\mathcal{H}_{\ell_2 0 \lambda_2 \mu_2}^{\Lambda_2}(t_2), \mathcal{H}_{\ell_1 0 \lambda_1 \mu_1}^{\Lambda_1}(t_1)] \\ \times (2i\tau_E)^{-1} \int_0^{\tau_E} dt_2 \int_0^{t_2} dt_1 \Sigma_{\lambda_2 \mu_2 \lambda_1 \mu_1}(t_2, t_1), \end{aligned} \quad (179)$$

where

$$\Sigma_{\lambda_2 \mu_2 \lambda_1 \mu_1}(t_2, t_1) = P^{-1} \sum_{p_2=0}^{P-1} \sum_{p_1=0}^{p_2} \sigma_{\lambda_2 \mu_2}(\hat{T}_{p_2} t_2) \sigma_{\lambda_1 \mu_1}(\hat{T}_{p_1} t_1). \quad (180)$$

The sums $\Sigma_{\lambda \mu}$ and $\Sigma_{\lambda_2 \mu_2 \lambda_1 \mu_1}$ vanish in certain cases, depending on the symmetry of the pulse sequence and the rotational signatures of the Hamiltonian terms. This leads to *symmetry-derived selection rules* for the average Hamiltonian terms of symmetrical pulse sequences. Some common cases are now examined in turn.

2. Antipalindromic expansion

In a stationary sample, antipalindromic expansion of an element \mathcal{E} leads to palindromic symmetry of the interaction-frame Hamiltonian [see Eq. (151)] as follows:

$$S = \hat{\mathbf{G}}_{\text{antipal}}^{(2)} \cdot \mathcal{E}:$$

$$\tilde{\mathcal{H}}_i(t, 0) = \tilde{\mathcal{H}}_i(\tau_S - t, 0) \quad (\text{stationary sample}). \quad (181)$$

An important result follows from this: all *even*-numbered average Hamiltonian terms vanish:

$$\bar{\mathcal{H}}_i^{(n)}(\hat{\mathbf{G}}_{\text{antipal}}^{(2)} \cdot \mathcal{E}) = 0 \quad (\text{stationary sample; even } n). \quad (182)$$

This is one of the earliest symmetry theorems in NMR pulse-sequence design.⁷ A proof is given in several places, including Haeberlen.¹³

The destruction of all even-order average Hamiltonian terms leads to a considerable improvement in the perfor-

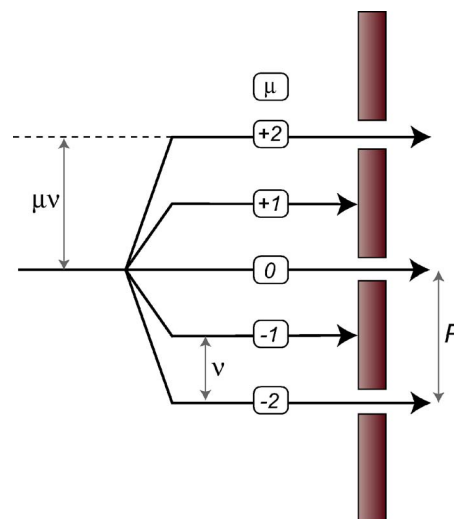


FIG. 4. (Color online) Selection rule diagram for the phase-step expansion of a cycle element, $S = \hat{\mathbf{G}}_{\Phi}^{\nu}(P) * \mathcal{C}$. A term with $\lambda=2$ is shown, with a set of components with spin quantum numbers $\mu \in \{-2, -1, \dots, +2\}$. The only symmetry-allowed components have $\mu\nu$ equal to an integer multiple of P .

mance of many pulse sequences, and is a staple of pulse-sequence design, especially in the NMR of stationary solids. For example, the performance of the Lee–Goldburg homonuclear decoupling method³ was vastly improved by imposing antipalindromic symmetry using longitudinal field jumps⁶¹ or phase-coherent frequency jumps,^{62,63} or by mimicking the frequency jumps by using phase stepping.⁶⁴ The good performance of the early homonuclear decoupling sequences such as WAHUHA (Refs. 6 and 13) and MREV8 (Refs. 7 and 14) owes much to the antipalindromic symmetry of these sequences.

3. Phase stepping of a cycle

A phase-step expansion of a cycle leads to the Euler angle symmetries given in Eq. (129). These lead to the following periodic relationship:

$$S = \hat{\mathbf{G}}_{\Phi}^{\nu}(P) * \mathcal{C}: \sigma_{\lambda \mu}(t_p) = \sigma_{\lambda \mu}(t_0) \exp\{-i\mu 2\pi \nu p/P\}. \quad (183)$$

The sum $\Sigma_{\lambda \mu}$ is therefore given by

$$\Sigma_{\lambda \mu}(t_0) = \sigma_{\lambda \mu}(t_0) \left\{ P^{-1} \sum_{p=0}^{P-1} \exp\{-i\mu 2\pi \nu p/P\} \right\}. \quad (184)$$

This vanishes unless $\mu\nu$ is an integer multiple of P (for a proof, see, for example, Ref. 2). This leads to the following selection rule for stationary samples:

$$\bar{\mathcal{H}}_{\ell 0 \lambda \mu}^{\Lambda(1)}(\hat{\mathbf{G}}_{\Phi}^{\nu}(P) * \mathcal{C}) = 0 \quad \text{if } \mu\nu \neq KP, \quad (185)$$

where K is an integer. A pictorial representation of this selection rule is shown in Fig. 4. A barrier with holes separated by P units suppresses an average Hamiltonian term unless the quantum number μ multiplied by the winding number ν coincides with a hole position.

A similar selection rule may be proved^{16,17,48,86} for the second-order terms as follows:

$$\bar{\mathcal{H}}_{\ell_2 0 \lambda_2 \mu_2 \ell_1 0 \lambda_1 \mu_1}^{\Lambda_2 \Lambda_1 (2)} (\hat{\mathbf{G}}_{\Phi}^{\nu}(P) * \mathcal{C}) = 0 \quad \text{if} \quad \begin{cases} \mu_2 \nu \neq KP \\ \mu_1 \nu \neq K'P \\ (\mu_2 + \mu_1) \nu \neq K''P, \end{cases} \quad (186)$$

where K , K' , and K'' are integers. Selection rules for higher-order terms are easily derived. They include an increasing number of Boolean conditions on the quantum numbers and the pulse-sequence symmetry numbers ν and P . In general, an average Hamiltonian term of order J vanishes unless any sum of up to J quantum numbers μ , multiplied by the winding number ν , is an integer multiple of the expansion order P .

The selection rule in Eq. (185) is used extensively in the design of pulse sequences for order-selective multiple-quantum excitation.^{16,17} An example in the context of homonuclear decoupling is given by the MSHOT-3 cycle,^{87,88} which uses a phase step with $P=3$ and $\nu=1$ in order to eliminate all interaction terms with $\mu = \pm 1$ and $\mu = \pm 2$ in the first-order average Hamiltonian, for static or slowly spinning samples.

A common special case is when $P=2$ and $\nu=1$, i.e., a cycle is repeated with a phase shift of π . In this case $\bar{\mathcal{H}}_{\ell 0 \lambda \mu}^{\Lambda (1)}$ vanishes for all components with odd values of the quantum number μ .

The second-order selection rule in Eq. (186) has been used to design sequences for the selective excitation of high multiple-quantum orders in solids and liquid crystals.^{16,17}

4. Fourfold decoupling sequence expansion

Now consider the fourfold expansion of an \mathcal{R} -element according to the procedure in Eq. (143). The Euler angles for the excitation field are related by the symmetries given in Eq. (144). This leads to the following relationships:

$$\begin{aligned} \sigma_{\lambda \mu}(t_2) &= (-1)^{\mu} \sigma_{\lambda \mu}(t_0), \\ \sigma_{\lambda \mu}(t_3) &= (-1)^{\mu} \sigma_{\lambda \mu}(t_1). \end{aligned} \quad (187)$$

This implies that the sum $\sum_{\lambda \mu}$ must vanish for odd values of μ . In addition, the following Wigner matrix symmetry:

$$d_{\mu \mu'}^{\lambda}(\pi + \beta) = (-1)^{\lambda + \mu'} d_{\mu - \mu'}^{\lambda}(\beta) \quad (188)$$

leads to the additional relationships

$$\begin{aligned} \sigma_{\lambda 0}(t_1) &= (-1)^{\lambda} \sigma_{\lambda 0}(t_0), \\ \sigma_{\lambda 0}(t_3) &= (-1)^{\lambda} \sigma_{\lambda 0}(t_2). \end{aligned} \quad (189)$$

This implies that the sum $\sum_{\lambda 0}$ must vanish for odd values of λ .

If $\lambda=1$, the only possible values of μ are 0 and ± 1 . The $\mu=0$ term vanishes through Eq. (189), while the $\mu = \pm 1$ terms vanish through Eq. (187). Therefore, the fourfold expansion in Eq. (143) averages to zero all terms that behave as first-rank tensors under rotations of the spins as follows:

$$\bar{\mathcal{H}}_{\ell 0 \lambda \mu}^{\Lambda (1)} (\hat{\mathbf{G}}_{\pi}(2) * \hat{\mathbf{G}}_{\text{rep}}(2) * \mathcal{R}) = 0 \quad \text{if } \lambda = 1. \quad (190)$$

First-rank spin interactions include chemical shift terms and also interactions with different spin species, providing that

these are not subjected to any resonant rf fields at the same time. This is why the fourfold expansion $\hat{\mathbf{G}}_{\pi}(2) * \hat{\mathbf{G}}_{\text{rep}}(2) * \mathcal{R}$ is the basis of many heteronuclear decoupling sequences in liquids.^{18–20,22–24}

B. Rotating solids

When a solid undergoes mechanical reorientation with respect to the external magnetic field, the high-field interaction terms $\mathcal{H}_{\ell 0 \lambda 0}^{\Lambda}$ are no longer time independent. The high-field spin Hamiltonian terms may be expressed as follows:

$$\mathcal{H}_{\ell 0 \lambda \mu}^{\Lambda}(t) = \sum_{m=-\ell}^{+\ell} \mathcal{H}_{\ell m \lambda 0}^{\Lambda} D_{m0}^{\ell}(\Omega_{RL}(t)), \quad (191)$$

where Ω_{RL} indicates the set of Euler angles relating the rotor frame R (fixed with respect to the sample holder) and the laboratory frame L (fixed with respect to the magnetic field). These Euler angles are time dependent for a rotating sample. For the common case of rotation at a constant angular frequency ω_r about an axis that subtends a fixed angle β_{RL} with respect to the magnetic field, the Euler angle $\alpha_{RL}(t)$ has a linear time dependence and is given by

$$\alpha_{RL}(t) = \alpha_{RL}^0 - \omega_r t. \quad (192)$$

The Euler angle γ_{RL} has no relevance in high magnetic field and may be ignored. The angle α_{RL}^0 represents the phase of the rotor at time $t=0$. For the common case of magic-angle spinning, β_{RL} is equal to $\arctan \sqrt{2} \cong 54.74^\circ$.

More complicated mechanical rotations may be used in certain circumstances, for example, double rotation.^{89–91}

If an excitation pulse sequence is applied at the same time as the sample rotation, the mechanical motion may also be included in the expressions for the interaction-frame Hamiltonians. In this case the interaction-frame Hamiltonian is written as follows:

$$\tilde{\mathcal{H}}_i(t) = \sum_{\Lambda, \ell, m, \lambda, \mu} \tilde{\mathcal{H}}_{\ell m \lambda \mu}^{\Lambda}(t), \quad (193)$$

where

$$\tilde{\mathcal{H}}_{\ell m \lambda \mu}^{\Lambda}(t) = \mathcal{H}_{\ell m \lambda \mu}^{\Lambda} \sigma_{\lambda \mu}^{\ell m}(t) \quad (194)$$

and

$$\sigma_{\lambda \mu}^{\ell m}(t) = \sigma^{\ell m}(t) \sigma_{\lambda \mu}(t). \quad (195)$$

Here $\sigma_{\lambda \mu}(t)$ is defined in Eq. (175). The analogous term for the spatial rotation is defined as follows:

$$\sigma^{\ell m}(t) = \exp\{-im\alpha_{RL}(t)\} d_{m0}^{\ell}(\beta_{RL}(t)). \quad (196)$$

If a suitable excitation pulse sequence is synchronized with the sample rotation, the doubly modulated term $\sigma_{\lambda \mu}^{\ell m}(t)$ becomes periodic. The imposed selection rules then depend on the spatial quantum numbers ℓ and m as well as the spin quantum numbers λ and μ .

Suppose that a pulse sequence is generated by N -fold symmetry expansion of an element \mathcal{E} , i.e., $S = \hat{\mathbf{G}}(N) * \mathcal{E}$, and that the full sequence S is timed to coincide with n rotational periods, where n is an integer. The first two average Hamiltonian terms are given by

$$\bar{\mathcal{H}}_i^{(1)}(S) = \sum_{\Lambda, \ell, m, \lambda, \mu} \bar{\mathcal{H}}_{\ell m \lambda \mu}^{\Lambda(1)}(S), \quad (197)$$

$$\bar{\mathcal{H}}_i^{(2)}(S) = \sum_{\Lambda_2, \ell_2, m_2, \lambda_2, \mu_2} \sum_{\Lambda_1, \ell_1, m_1, \lambda_1, \mu_1} \bar{\mathcal{H}}_{\ell_2 m_2 \lambda_2 \mu_2 \ell_1 m_1 \lambda_1 \mu_1}^{\Lambda_2 \Lambda_1(2)}(S),$$

where the first-order term is given by

$$\bar{\mathcal{H}}_{\ell m \lambda \mu}^{\Lambda(1)}(S) = \mathcal{H}_{\ell m \lambda \mu}^{\Lambda} \times \tau_E^{-1} \int_0^{\tau_E} dt \Sigma_{\lambda \mu}^{\ell m}(t) \quad (198)$$

and

$$\Sigma_{\lambda \mu}^{\ell m}(t) = N^{-1} \sum_{p=0}^{N-1} \sigma_{\lambda \mu}^{\ell m}(\hat{T}_p t). \quad (199)$$

Here $\sigma_{\lambda \mu}^{\ell m}$ is defined in Eq. (195). Similarly, the second-order term is given by

$$\begin{aligned} \bar{\mathcal{H}}_{\ell_2 m_2 \lambda_2 \mu_2 \ell_1 m_1 \lambda_1 \mu_1}^{\Lambda_2 \Lambda_1(2)}(S) \\ = [\mathcal{H}_{\ell_2 m_2 \lambda_2 \mu_2}^{\Lambda_2}(t_2), \mathcal{H}_{\ell_1 m_1 \lambda_1 \mu_1}^{\Lambda_1}(t_1)] \\ \times (2i\tau_E)^{-1} \int_0^{\tau_E} dt_2 \int_0^{t_2} dt_1 \Sigma_{\lambda_2 \mu_2 \lambda_1 \mu_1}^{\ell_2 m_2 \ell_1 m_1}(t_2, t_1), \end{aligned} \quad (200)$$

where

$$\Sigma_{\lambda_2 \mu_2 \lambda_1 \mu_1}^{\ell_2 m_2 \ell_1 m_1}(t_2, t_1) = N^{-1} \sum_{p_2=0}^{N-1} \sum_{p_1=0}^{p_2} \sigma_{\lambda_2 \mu_2}^{\ell_2 m_2}(\hat{T}_{p_2} t_2) \sigma_{\lambda_1 \mu_1}^{\ell_1 m_1}(\hat{T}_{p_1} t_1). \quad (201)$$

The symmetry of the pulse sequence and the mode of synchronization with the sample rotation can cause the sums $\Sigma_{\lambda \mu}^{\ell m}$ and $\Sigma_{\lambda_2 \mu_2 \lambda_1 \mu_1}^{\ell_2 m_2 \ell_1 m_1}$ to vanish, for certain combinations of quantum numbers. This leads to selection rules for the average Hamiltonian components.

1. Antipalindromic symmetry

Antipalindromic symmetry is not very useful for the design of pulse sequences applied to rotating solids, since the modulation of the spin interaction terms by the sample rotation destroys the essential symmetry relationship in Eq. (181). The even-numbered average Hamiltonian terms of antipalindromic sequences applied to rotating samples do *not* vanish, in general.

In principle, the necessary symmetry in the internal Hamiltonians could be restored by instantaneously reversing the sense of the sample rotation—but this is not mechanically feasible.

2. CN_n^ν symmetry

Pulse sequences in the symmetry class CN_n^ν are constructed by synchronizing an excitation sequence of the form $\hat{G}_\Phi^\nu(N) * \mathcal{C}$ with n rotation periods of the sample, where n is an integer, i.e.,

$$CN_n^\nu = \frac{\hat{G}_\Phi^\nu(N) * \mathcal{C}}{n \text{ rotor periods}}. \quad (202)$$

In this context, the number of complete phase rotations ν is

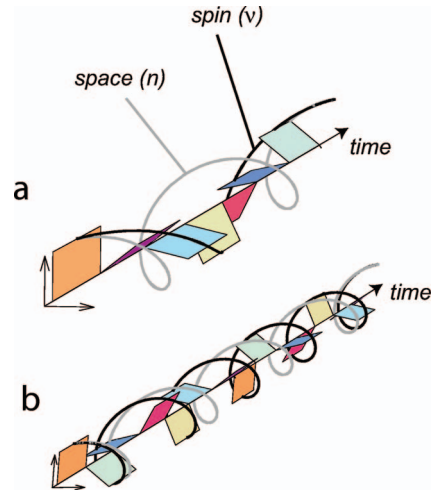


FIG. 5. (Color) Graphical representation of CN_n^ν symmetries. The black spiral indicates the circulation of the radio-frequency phases, while the gray spiral indicates the sample rotation. (a) A sequence with $C7_2^1$ symmetry; (b) a sequence with $C14_4^5$ symmetry.

known as the *spin winding number*, and the number of complete sample rotations n is known as the *space winding number*. Figure 5 provides a graphical representation of the space-spin symmetries of CN_n^ν sequences.

The spin terms $\sigma_{\lambda \mu}(t)$ have the symmetry appropriate for a phase-stepped cycle, as given in Eq. (183) as follows:

$$CN_n^\nu: \sigma_{\lambda \mu}(t_p) = \sigma_{\lambda \mu}(t_0) \exp\{-i2\pi\mu\nu p/N\}. \quad (203)$$

From Eqs. (192) and (196), the space terms $\sigma^{\ell m}(t)$ have the following symmetry:

$$\begin{aligned} \sigma^{\ell m}(t_p) &= \sigma^{\ell m}(t_0) \exp\{+im\omega_r(t_p - t_0)\} \\ &= \sigma^{\ell m}(t_0) \exp\{+im\omega_r n p \tau_E\} \\ &= \sigma^{\ell m}(t_0) \exp\{+i2\pi mn p/N\}. \end{aligned} \quad (204)$$

These equations lead to the following symmetry of the combined space-spin terms:

$$\sigma_{\lambda \mu}^{\ell m}(t_p) = \sigma_{\lambda \mu}^{\ell m}(t_0) \exp\{i2\pi(mn - \mu\nu)p/N\}. \quad (205)$$

The sum $\Sigma_{\lambda \mu}^{\ell m}$ is therefore given by

$$\Sigma_{\lambda \mu}^{\ell m}(t_0) = \sigma_{\lambda \mu}^{\ell m}(t_0) \left\{ N^{-1} \sum_{p=0}^{N-1} \exp\{i2\pi(mn - \mu\nu)p/N\} \right\}. \quad (206)$$

This vanishes unless $mn - \mu\nu$ is an integer multiple of N . The following selection rule follows:

$$\bar{\mathcal{H}}_{\ell m \lambda \mu}^{\Lambda(1)}(CN_n^\nu) = 0 \quad \text{if } mn - \mu\nu \neq KN, \quad (207)$$

where K is an integer. This selection rule is similar to that given for stationary samples in Eq. (185), except for the participation of the space quantum number m and space symmetry number n , as well as the spin quantum numbers. A diagrammatic representation of this selection rule is shown in Fig. 6.

Similar selection rules follow for the higher-order terms, for example,

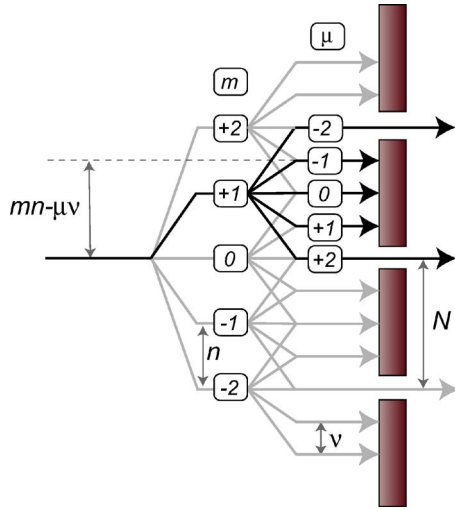


FIG. 6. (Color online) Selection rule diagram for a CN_n^ν sequence. A term with $\ell=\lambda=2$ is shown, with a set of components with space quantum numbers $\mu \in \{-2, -1 \dots +2\}$ and spin quantum numbers $m \in \{-2, -1 \dots +2\}$. The terms with $m=+1$ are highlighted. The only symmetry-allowed components have $\mu - \mu\nu$ equal to an integer multiple of N . The example shown corresponds to $C4_2^1$. The diagram shows that the first-order average Hamiltonian terms with $\{m, \mu\} = \{+1, -2\}$ and $\{+1, +2\}$ are symmetry allowed in this case.

$$\bar{\mathcal{H}}_{\ell_2 m_2 \lambda_2 \mu_2 \ell_1 m_1 \lambda_1 \mu_1}^{\Lambda_2 \Lambda_1 (2)}(CN_n^\nu) = 0 \quad \text{if} \quad \begin{cases} m_2 n - \mu_2 \nu \neq KN \\ m_1 n - \mu_1 \nu \neq K'N \\ (m_2 + m_1)n - (\mu_2 + \mu_1)\nu \neq K''N, \end{cases} \quad (208)$$

where K , K' , and K'' are integers.

3. RN_n^ν symmetry

Pulse sequences in the symmetry class RN_n^ν are constructed by synchronizing an excitation sequence of the form $\hat{\mathbf{G}}_{\text{rep}}(N/2) * \hat{\mathbf{G}}_\sigma(2) * \hat{\Phi}(\pi\nu/N) \cdot \mathcal{R}_0$ with n rotation periods of the sample, where n is an integer, and N is an even integer, i.e.

$$RN_n^\nu = \underbrace{\hat{\mathbf{G}}_{\text{rep}}(N/2) * \hat{\mathbf{G}}_\sigma(2) * \hat{\Phi}(\pi\nu/N) \cdot \mathcal{R}_0}_{n \text{ rotor periods}}. \quad (209)$$

The Euler angle symmetries for the excitation field are given in Eq. (146). These lead to the following symmetries of the spin terms:

$$\sigma_{\lambda\mu}(t_p) = (-1)^{p\lambda} \sigma_{\lambda\mu}(t_0) \exp\{-i2\pi\mu\nu p/N\} \quad (210)$$

and hence the following symmetry of the combined space-spin terms:

$$\sigma_{\lambda\mu}^\ell(t_p) = (-1)^{p\lambda} \sigma_{\lambda\mu}^\ell(t_0) \exp\{i2\pi p(mn - \mu\nu)/N\}, \quad (211)$$

which may be written as follows:

$$\sigma_{\lambda\mu}^\ell(t_p) = \sigma_{\lambda\mu}^\ell(t_0) \exp\{i2\pi p(mn - \mu\nu + N\lambda/2)\}. \quad (212)$$

This leads to the following first-order selection rule:

$$\bar{\mathcal{H}}_{\ell m \lambda \mu}^{\Lambda (1)}(RN_n^\nu) = 0 \quad \text{if} \quad mn - \mu\nu + N\lambda/2 \neq KN, \quad (213)$$

which may be formulated more conveniently as follows:

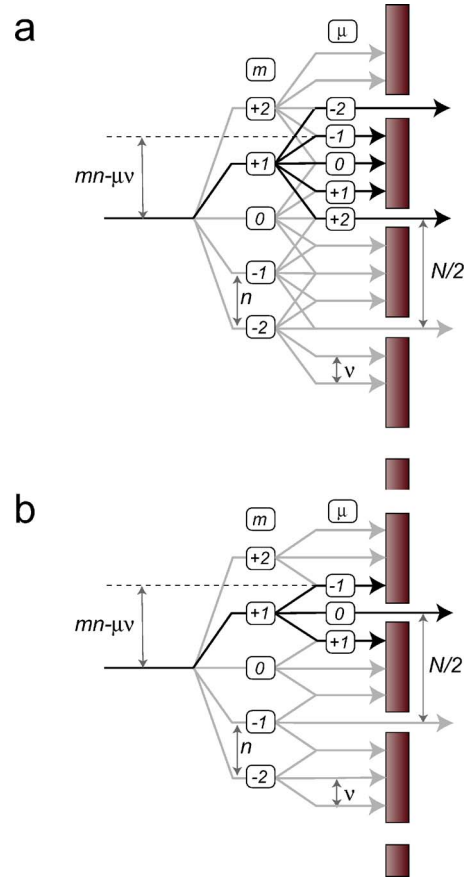


FIG. 7. (Color online) Selection rule diagrams for a RN_n^ν sequence. The example shown corresponds to $R8_2^1$. Diagram (a) is appropriate for an even value of λ . A term with $\ell=\lambda=2$ is shown, with a set of components with space quantum numbers $\mu \in \{-2, -1 \dots +2\}$ and spin quantum numbers $m \in \{-2, -1 \dots +2\}$. The terms with $m=+1$ are highlighted. The only symmetry-allowed components have $\mu - \mu\nu$ equal to an even multiple of $N/2$. The terms with $\{m, \mu\} = \{+1, -2\}$ and $\{+1, +2\}$ are symmetry allowed. Diagram (b) is appropriate for an odd value of λ . A term with $\ell=2$ and $\lambda=1$ is shown, with a set of components with space quantum numbers $\mu \in \{-1, 0, +1\}$ and spin quantum numbers $m \in \{-2, -1 \dots +2\}$. The terms with $m=+1$ are highlighted. The only symmetry-allowed components have $\mu - \mu\nu$ equal to an odd multiple of $N/2$. The term with $\{m, \mu\} = \{+1, 0\}$ is symmetry allowed.

$$\bar{\mathcal{H}}_{\ell m \lambda \mu}^{\Lambda (1)}(RN_n^\nu) = 0 \quad \text{if} \quad mn - \mu\nu \neq K_\lambda N/2, \quad (214)$$

where K_λ is an integer with the same parity as λ , i.e., if λ is an odd integer, then K_λ is odd, while if λ is even, then K_λ is an even integer. A diagrammatic representation of this selection rule is shown in Fig. 7.

Similar selection rules apply to the higher-order terms, for example,

$$\begin{aligned} \bar{\mathcal{H}}_{\ell_2 m_2 \lambda_2 \mu_2 \ell_1 m_1 \lambda_1 \mu_1}^{\Lambda_2 \Lambda_1 (2)}(RN_n^\nu) \\ = 0 \quad \text{if} \quad \begin{cases} m_2 n - \mu_2 \nu \neq K_{\lambda_2} N/2 \\ m_1 n - \mu_1 \nu \neq K_{\lambda_1} N/2 \\ (m_2 + m_1)n - (\mu_2 + \mu_1)\nu \neq K_{\lambda_2 + \lambda_1} N/2, \end{cases} \end{aligned} \quad (215)$$

where K_{λ_2} is an integer of the same parity as λ_2 , K_{λ_1} is an integer of the same parity as λ_1 , and $K_{\lambda_2 + \lambda_1}$ is an integer of the same parity as $\lambda_2 + \lambda_1$.

4. Dual symmetries

Synchronized pulse sequences may be used simultaneously on two or more radio-frequency channels in order to impose selection rules that concern more than one spin species. For example, the notation $CN_n^{\nu I, \nu S}$ is used to indicate simultaneous $CN_n^{\nu I}$ and $CN_n^{\nu S}$ sequences on the I and S -spin channels, while the notation $CRN_n^{\nu I, \nu S}$ is used to indicate simultaneous $CN_n^{\nu I}$ and $RN_n^{\nu S}$ sequences on the I and S -spin channels. The selection rules for these dual sequences are given in Ref. 92.

5. Examples

The selection rules generated by CN_n^{ν} and RN_n^{ν} symmetries are very versatile and have been used for a wide variety of purposes in solid-state NMR. Some of these implementations were already in existence before the general theory of CN_n^{ν} and RN_n^{ν} sequences was developed. A review of the earlier literature, and tables of symmetry numbers for various applications, is given in Ref. 76.

A partial summary of the literature on symmetry-based sequences in rotating solids is given in Table III.

IX. HIGHER-LEVEL SYMMETRY EXPANSIONS

A. Supercycles

A sequence constructed according to the principles described above may be expanded further by applying further-sets of sequence modifiers. In some cases this renders the pulse sequence more robust with respect to various experimental imperfections, or reduces higher-order terms which are not controlled completely by the original sequence.

The principle has been used extensively in NMR sequence development for a long time. Consider, for example, the windowless BLEW12 sequence, which is a power-efficient method of achieving homonuclear dipolar decoupling in static or slowly rotating solids.⁹³ This pulse sequence may be written concisely as follows:

$$\text{BLEW12} = \hat{\mathbf{G}}_{\text{antipal}} * \{\hat{E}, \hat{\sigma}_{xz}, \hat{E}\} * 90_{90} 90_{0}. \quad (216)$$

Supercycles are also very useful for rotor-synchronized pulse sequences. Consider, for example, the xy8 phase cycle which has been used for a long time to stabilize REDOR experiments.⁹⁴ The phase-cycled REDOR sequence uses 180° pulse trains, with consecutive pulses separated by one-half of a rotor period, and with phases given by repeating the palindromic sequence: $\{0^\circ, 90^\circ, 0^\circ, 90^\circ, 90^\circ, 0^\circ, 90^\circ, 0^\circ\}$. This may be interpreted as a mirror-pair supercycle of a $R4_2^1$ sequence as follows:

$$\text{xy8} = \hat{\Phi}(-\pi/4) \cdot \hat{\mathbf{G}}_{\sigma}(2) * R4_2^1, \quad (217)$$

where the \mathcal{R} -element is equal to a single strong 180° pulse followed by half a rotor period of free evolution. The $-\pi/4$ phase shift in Eq. (217) is only required for consistency with the historical implementation and could be omitted.

A more recent example is provided by the robust SR26 pulse sequence which is useful for relatively long-range

double-quantum homonuclear recoupling, and has been used to elucidate the network structures of zeolites.^{95,96} The pulse sequence structure is as follows:

$$\text{SR26} = \{\hat{E}, \hat{\sigma}_{xz}, \hat{\sigma}_{xz}, \hat{\Phi}(\pi), \hat{\Phi}(\pi)\} * R26_4^{11}. \quad (218)$$

A detailed discussion of symmetry-based supercycles, with some powerful theorems for the average Hamiltonian terms, is found in Ref. 47. An explicit theory of the SR26 supercycle may be found in Ref. 38.

B. Iterative expansions

Suppose that a symmetrical expansion is applied repetitively to a certain pulse sequence, i.e.,

$$S^{(1)} = \hat{\mathbf{G}}(P) * S^{(0)}, \quad (219)$$

$$S^{(2)} = \hat{\mathbf{G}}(P) * S^{(1)},$$

and so on. At each stage of the expansion, the rf propagator will be different. However, in some special cases, a remarkable thing happens. On each iteration, the propagators get closer and closer to a *fixed point* in propagator space.⁹⁷ This happens if (i) the expansion operator $\hat{\mathbf{G}}(P)$ fulfills certain mathematical conditions, and (ii) the starting point of the iteration, namely, the element \mathcal{E} , falls within the *basin* of the expansion. Such expansions allow one to construct accurate propagators for the nuclear spins, even when the rf elements themselves are highly inaccurate. The mathematical principles of this method have been described thoroughly in the literature⁹⁷ and only a few representative examples are given here.

1. Iterative cycle construction

Accurate rf cycles may be constructed by an iteration of order 4, as follows:

$$\hat{\mathbf{G}}(4) = \{\hat{E}, \hat{\mathcal{C}}^+(\mathcal{R})\} * \hat{\mathbf{G}}_{\pi}. \quad (220)$$

Repetition of the sequence with a π phase shift is followed by repetition and cyclic permutation of a \mathcal{R} -element. As an example, consider a starting cycle constructed by repeating two \mathcal{R} -elements with phase $\phi=0$ as follows.

$$S^{(0)} = \hat{\mathbf{G}}_{\text{rep}}(2) * \mathcal{R}_0 = \mathcal{R}_0 \mathcal{R}_0. \quad (221)$$

The iteration proceeds as follows:

$$\begin{aligned} S^{(1)} &= \{\hat{E}, \hat{\mathcal{C}}^+(\mathcal{R})\} * \hat{\mathbf{G}}_{\pi} * S^{(0)} \\ &= \mathcal{R}_0 \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_{\pi} \mathcal{R}_0, \end{aligned} \quad (222)$$

$$\begin{aligned} S^{(2)} &= \{\hat{E}, \hat{\mathcal{C}}^+(\mathcal{R})\} * \hat{\mathbf{G}}_{\pi} * S^{(1)} \\ &= \mathcal{R}_0 \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_{\pi} \mathcal{R}_0 \\ &\quad - \mathcal{R}_{\pi} \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_{\pi} \\ &\quad - \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_{\pi} \\ &\quad - \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_0 \mathcal{R}_0 \mathcal{R}_{\pi} \mathcal{R}_0, \end{aligned}$$

and so on. On each stage, the overall propagator gets closer

TABLE III. Some literature examples of CN_n^ν and RN_n^ν sequences.

Symmetry	Supercycle	Application	Common acronym	Publication date	Reference
$C5_1^1$	Involves insertion of π pulse	Emulation of zero-field NMR in high field	ZFHF	1988	74 and 75
$R4_2^0$...	Heteronuclear recoupling	REFOR	1989	49 and 50
$R4_2^1$	$\hat{G}_\sigma(2)$	Heteronuclear recoupling	REDOR-xy8	1991	94
$R2_2^0$...	Zero-quantum homonuclear recoupling	RFDR	1992	29 and 30
$C7_2^1$...	Double-quantum homonuclear recoupling	C7	1995	31
$C3_1^0, C4_1^0$...	Homonuclear decoupling under fast magic-angle spinning	...	1995	65
$R6_1^0, R8_1^0$...	Selection of J -couplings	TOBSY	1996	70
$C7_1^2$...	Double-quantum homonuclear recoupling	POST-C7	1998	32
$R24_2^1$...	Heteronuclear decoupling with homonuclear recoupling	R24	1999	86
$C5_2^1$	\hat{G}_π	Double-quantum homonuclear recoupling	SPC5	1999	34
$C14_4^5$	Complicated	Double-quantum homonuclear recoupling	SC14	2000	33
$R14_2^6$...	Double-quantum homonuclear recoupling	R14	2000	36
$C3_3^1, C7_7^1$...	Heteronuclear recoupling with homonuclear decoupling	C-REDOR	2001	53
$C9_3^1, C9_6^1$, etc.	...	Selection of J -couplings	C-TOBSY	2001	71
$R30_6^{14}$, etc.	...	Selection of J -couplings	R-TOBSY	2001	72
$R18_1^7, R18_2^5$...	Heteronuclear recoupling with homonuclear decoupling	R18, PRESTO	2001	51 and 52
$R24_9^{8,7}$, etc.	...	Dual recoupling	...	2001	92
$R18_2^9$...	Homonuclear decoupling	...	2001	66
$R16_6^5, R18_8^5$, etc.	...	Double-quantum homonuclear recoupling	...	2002	39
$R4_4^1, R6_6^2$, etc.	$\hat{G}_\Phi^1(3)*\hat{G}_\sigma(2)$	Zero-quantum homonuclear recoupling	...	2002	46
$C7_2^1$, etc.	...	Band-selective homonuclear recoupling	...	2003	44
$R26_4^{11}$	$\{\hat{E}, \hat{\sigma}_{xz}, \hat{\sigma}_{xz}\hat{\Phi}(\pi), \hat{\Phi}(\pi)\}$	Double-quantum homonuclear recoupling	SR26	2004	37 and 38
$R18_3^7$, etc.	$\hat{G}_\Phi^1(3)*\hat{G}_\sigma(2)$	Triple-quantum homonuclear recoupling	...	2004	47 and 48
$R20_2^9$...	Double-quantum homonuclear recoupling	...	2005	41
$C3_3^1$...	Simultaneous CSA and homonuclear recoupling	TDR	2006	35
$C7_2^1$...	Band-selective homonuclear recoupling	SEASHORE	2006	45
$R12_3^5$, etc.	$\hat{G}_\Phi^1(3)*\hat{G}_\sigma(2)$	Heteronuclear recoupling with homonuclear decoupling	...	2006	55
$R4_1^2$	$\hat{G}_\Phi^1(3)*\hat{G}_\sigma(2)$	Heteronuclear recoupling with homonuclear decoupling	...	2006	54
$R18_2^5, R12_5^4$...	CSA recoupling with homonuclear decoupling	...	2007	59 and 60

to that of an exact cycle, even if the starting element is highly nonideal. This procedure has been used to construct accurate heteronuclear decoupling sequences in solution NMR.^{18–20} A similar procedure exists which involves the permutation of \mathcal{P} -elements instead of \mathcal{R} -elements.^{21,22}

2. Iterative \mathcal{R} -element construction

Accurate \mathcal{R} -elements may be constructed by iterative application of a fivefold phase-step expansion to an initial \mathcal{R} -element as follows:

$$\hat{G}(5) = \{\hat{\Phi}(\varphi_1), \hat{\Phi}(\varphi_2), \hat{\Phi}(\varphi_3), \hat{\Phi}(\varphi_4), \hat{\Phi}(\varphi_5)\}. \quad (223)$$

The phases $\{\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5\}$ must obey certain conditions, which have been elucidated by Pines and co-workers.^{98,99}

One suitable set of phases is as follows (given in degrees):

$$\{\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5\} = \{0, 0, 120, 60, 120\}. \quad (224)$$

Repeated application of this expansion to a starting element $\mathcal{R}_0 = 180_0$ leads to the following 25-pulse sequence:

$$\begin{aligned} \hat{G}(5) * \hat{G}(5) * 180_0 = & 180_0 180_0 180_{120} 180_{60} 180_{120} \\ & - 180_0 180_0 180_{120} 180_{60} 180_{120} \\ & - 180_{120} 180_{120} 180_{240} 180_{180} 180_{240} \\ & - 180_{60} 180_{60} 180_{180} 180_{120} 180_{180} \\ & - 180_{120} 180_{120} 180_{240} 180_{180} 180_{240}. \end{aligned} \quad (225)$$

This is a highly robust \mathcal{R} -element, compensated to a high degree for pulse imperfections.^{98,99}

Iterative schemes for constructing \mathcal{P} -elements also exist.¹⁰⁰

Pulse sequences constructed this way are highly symmetrical, although their symmetry is not usually apparent to the eye. In this respect they resemble fractal geometrical constructions, which also have a pseudorandom “natural” appearance, concealing a highly systematic internal structure.

X. CONCLUSIONS

The symmetry of NMR pulse sequences is a remarkably rich subject and many avenues are completely unexplored. My hope is that the current article at least provides a language which may be used to discuss the subject in the future.

Despite its length, this article is highly incomplete. Many topics related to the symmetry theory of NMR pulse sequences have *not* been covered here. These include the following.

- (1) Spatial symmetries of the nuclear spin interactions are utilized in numerous experiments, such as magic-angle spinning itself, as well as double-rotation and dynamic-angle spinning experiments.⁸⁹⁻⁹¹
- (2) Symmetries involving the orientational distribution of molecules in solid samples can be important. For example, the “carousel” symmetries in the orientational distribution of powders give rise to absorption-shape spectral lineshapes in magic-angle-spinning NMR spectra.^{101,102}
- (3) The response of NMR pulse sequences to sign changes in the controlling parameters often reflects the internal symmetry of the pulse sequence.¹⁰³
- (4) Many NMR pulse sequences involve an overall symmetrical construction that goes beyond the symmetry of the local pulse sequence blocks. For example, the excitation of multiple-quantum coherence by an initial pulse sequence is often matched by a symmetry-related closing pulse sequence. Proper matching of the two pulse sequences optimizes the overall signal amplitude.⁷⁹

- (5) Many NMR experiments involve repetition of the experiments with variation of phases and timings in a symmetrical pattern (“phase cycling”) in order to isolate certain classes of nuclear spin signals.^{2,104-108}

NMR pulse sequence design is part of a wider topic, namely, the dynamic control of quantum systems. The control of quantum dynamics by imposing symmetry on the experimental manipulations is a highly intriguing field of research which NMR spectroscopists may have wandered into almost by accident. As in many other cases, the insights from the symmetry theory of NMR pulse sequences may be useful as a template for the emerging methodology in other spectroscopic disciplines.

Despite the intellectual appeal of symmetry as a pulse-sequence design principle, the most efficient pulse sequences are not always symmetric ones. For example, the complex waveforms generated by optimal control algorithms often lack any recognizable pattern. Nevertheless they often display astonishingly robust control characteristics.¹⁰⁹⁻¹¹¹

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