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Theory of Multiple-Pulse NMR at Low and Zero Fields

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Coherent averaging with time-dependent magnetic fields at low and zero static magnetic fields encounters several features which are unfamiliar in high-field magnetic resonance. The principal differences are that magnetic field pulses act generally on all spin species in the sample and that the Hamiltonian contains additional terms that are normally discarded in a high static magnetic field. We illustrate how the full Hamiltonian or different terms of the Hamiltonian may be averaged to zero by sequences of 90° rotations around the x, y, and z axes. The two limiting cases of ideal delta-function pulses and windowless sequences are treated. We also show that the duality between rotations of space coordinates and spin coordinates allows one to replace spatial reorientations of the sample, such as magic-angle spinning, by time-dependent magnetic fields. Sequences of delta-function pulses at zero field are analogous to recursive expansion schemes of multiple-pulse sequences at high field. The terms of the full Hamiltonian appear also in the average Hamiltonian of high-field pulse sequences and can be manipulated by the same sequence of configurations as in zero-field multiple-pulse NMR.

INTRODUCTION

The principal sources of broadening of the resonance lines in solid-state NMR are strong dipolar interactions and, in disordered systems such as powders and amorphous solids, the superposition of different orientations, leading to inhomogeneously broadened resonance lines. The traditional approaches to overcome these broadening mechanisms and obtain high-resolution spectra in solids have been the use of multiple-pulse sequences to create effective average Hamiltonians by manipulating the spin operators (*1*) and rapid spinning (*2–4*) or hopping (*5*) of the sample around an axis tilted from the direction of the magnetic field by the "magic angle," $\Theta_m = 54.7°$ to average out those interactions that transform under spatial rotations like irreducible tensors of rank two, such as chemical shielding anisotropy. An alternative approach for the elimination of inhomogeneous broadening in dipolar- or quadrupolar-coupled spin systems is zero-field magnetic resonance (*6–11*). In the absence of a magnetic field all the spins experience the same interactions, independent of the orientation of the crystallite. Most forms of inhomogeneous line broadening therefore vanish in zero field while spin–spin couplings and quadrupolar interactions remain. The Hamiltonian of the spin system does not depend on the orientation of the individual crystallite and space becomes essentially isotropic from the point of view of magnetic resonance.

In this paper we discuss the possibilities of manipulating the spin degrees of freedom by applying sequences of magnetic field pulses in low or zero static magnetic fields.

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Possible goals are homonuclear and heteronuclear spin decoupling by multiple-pulse sequences and the use of composite pulses either to create homogeneous excitation of the spin system or to excite selectively only one spin species (*12*). While the internal Hamiltonian of a spin system at zero field is independent of the orientation of the crystallite or molecule, the direction of the time-dependent magnetic field breaks this full rotational symmetry. An arbitrary pulse sequence has therefore an effect on the spin system that depends on the relative orientation of the molecule and the magnetic field. The resulting spectrum will therefore display a powder pattern. This can be avoided by designing multiple-pulse sequences that generate an "isotropic" average Hamiltonian.

Because the total Hamiltonian is invariant under simultaneous rotations of the space and spin coordinates, it is always possible, at least in principle, to replace an experiment that includes sample reorientation, such as magic-angle spinning or hopping, by an equivalent experiment that leaves the orientation of the sample invariant but imposes an appropriate time dependence on the magnetic field. It is therefore possible to design experiments that average out interactions transforming as second-rank tensors under rotations of space coordinates without actually moving the sample. Three experiments will be discussed which are equivalent to magic-angle spinning in the high-field and low-field limits.

Multiple-pulse sequences designed for use at high magnetic fields cannot be used at low static fields since they take into account only the high-field, truncated, part of the Hamiltonian, including only interactions that are invariant under rotations around the magnetic field. It is therefore necessary to develop new pulse sequences that take into account the full, untruncated zero-field Hamiltonian. From the transformation properties under rotations of the spin coordinates of the additional terms we expect, as an additional benefit, some insight into the understanding of some high-field multiple-pulse experiments where the same terms appear as imperfections of the pulse sequence (*13, 14*). While multiple-pulse sequences at high magnetic fields use only rotations around the x and y axes of the rotating frame, zero-field magnetic resonance allows equally rotations around the z axis. In the iterative design of multiple-pulse sequences, the analogous operation is achieved by shifting the phase of the radiofrequency pulses, thereby rotating the average Hamiltonian around the z axis.

SPIN HAMILTONIANS

We consider a system of spins I at zero field or in a magnetic field that is too weak to effectively truncate dipole–dipole and quadrupolar interactions. The Hamiltonian of such a system contains the following terms:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_P(t) = \mathcal{H}_{int} + \mathcal{H}_P(t)$$

$$\mathcal{H}_1 = \sum_j -\gamma_j \mathbf{I}_j (1-\sigma_j)\mathbf{B}_0$$

$$\mathcal{H}_2 = \sum_j \sum_k \mathbf{I}_j \mathbf{D}_{jk} \mathbf{I}_k + \sum_j \mathbf{I}_j \mathbf{Q}_j \mathbf{I}_j$$

$$\mathcal{H}_P(t) = -\sum_j \gamma_j \mathbf{I}_j \cdot \mathbf{B}_P(t), \qquad [1]$$

where vectors are written as **V** and tensors as **T**, γ represents the gyromagnetic ratio, **I** the angular momentum operator, σ the chemical-shift tensor, $\mathbf{B}_0$ "static" magnetic fields, **D** the spin–spin coupling tensor, **Q** the interaction of the nuclear quadrupole moment with the electric field gradient tensor, and $\mathbf{B}_P(t)$ the pulsed magnetic field. $\mathscr{H}_1$ contains interactions linear in the spin operators and $\mathscr{H}_2$ terms bilinear in the spin operators, transforming like irreducible tensors of rank two if all the spin operators involved are rotated synchronously. The effect of the pulses, represented by $\mathscr{H}_P(t)$, is evaluated without taking the chemical shift into account, thus assuming that all the spins with the same gyromagnetic ratio are rotated through the same angle. We distinguish between the pulsed field $\mathbf{B}_P$ and the field $\mathbf{B}_0$ which is considered to be static or slowly varying on the time scale of the multiple-pulse sequence.

The coordinate system used is the laboratory-fixed frame of reference. We expand the linear part of the Hamiltonian in the basis of the single-spin operators and use the notation $X \equiv I_{jx}$, $Y \equiv I_{jy}$, and $Z \equiv I_{jz}$ and the bilinear terms in the basis $XX \equiv I_{jx}I_{kx} - (1/3)\mathbf{I}_j \cdot \mathbf{I}_k$, $YY \equiv I_{jy}I_{ky} - (1/3)\mathbf{I}_j \cdot \mathbf{I}_k$, $ZZ \equiv I_{jz}I_{kz} - (1/3)\mathbf{I}_j \cdot \mathbf{I}_k$, $XY \equiv I_{jx}I_{ky} + I_{jy}I_{kx}$, $XZ \equiv I_{jx}I_{kz} + I_{jz}I_{kx}$, and $YZ \equiv I_{jy}I_{kz} + I_{jz}I_{ky}$. The Hamiltonian can therefore be brought into the form

$$\mathscr{H}_{\text{int}} = \mathscr{H}_1 + \mathscr{H}_2 = \sum_j \sum_\alpha a_{j\alpha}\alpha + \sum_j \sum_k \sum_\alpha \sum_\beta b_{jk\alpha\beta}\alpha\beta, \qquad \alpha, \beta = X, Y, Z. \tag{2}$$

The coefficients $a_{j\alpha}$ and $b_{jk\alpha\beta}$ are functions of the orientation of the crystallite. In general the three linear terms are independent of each other, while the quadratic terms are related by

$$\sum_\alpha b_{jk\alpha\alpha} = 0, \tag{3}$$

leaving five independent bilinear terms, determined by the number of elements of an irreducible tensor of rank two.

Effect of pulses. Multiple-pulse NMR uses magnetic field pulses to make the Hamiltonian of the system appear time dependent, thereby averaging it to the desired form (*1*). The rotations of the spins induced by the magnetic field pulses alone are usually not of interest and the system is therefore observed at times t_d when the overall rotation vanishes. The propagator generated by the pulses alone is

$$U_P(t_d) = Te^{-i\int_0^{t_d}\mathscr{H}_P(t')dt'} = 1, \tag{4}$$

where T represents the Dyson time-ordering operator. It is therefore convenient to separate the effect of the pulses on the system from the evolution caused by the internal Hamiltonian and write the time dependence of the density operator as

$$\rho(t) = U_P(t)\tilde{U}_{\text{int}}(t)\rho(0)\tilde{U}^\dagger_{\text{int}}(t)U^\dagger_P(t), \tag{5}$$

so that the density operator at detection is determined by

$$\rho(t_d) = \tilde{U}_{\text{int}}(t_d)\rho(0)\tilde{U}^\dagger_{\text{int}}(t_d), \tag{6}$$

where the propagator of the interaction representation is given by

$$\tilde{U}_{\text{int}}(t) = Te^{-i\int_0^t \tilde{\mathscr{H}}_{\text{int}}(t')dt'} \tag{7}$$

and

$$\tilde{\mathscr{H}}_{\text{int}}(t) = U_{\text{P}}^{\dagger}(t)\mathscr{H}_{\text{int}}U_{\text{P}}(t). \qquad [8]$$

The internal Hamiltonian therefore appears time dependent under the influence of the magnetic field pulses. We will consider the operators as time dependent and the coefficients a and b as static:

$$\tilde{\mathscr{H}}_{\text{int}}(t) = \sum_j \sum_\alpha a_{j\alpha}\tilde{\alpha}(t) + \sum_j \sum_k \sum_\alpha \sum_\beta b_{jk\alpha\beta}\tilde{\alpha}(t)\tilde{\beta}(t) \qquad [9]$$

with

$$\tilde{\alpha}(t) = U_{\text{P}}^{\dagger}(t)\alpha U_{\text{P}}(t), \qquad \text{etc.} \qquad [10]$$

As long as only 90° rotations around the coordinate axes are considered, each operator is converted into another operator of the same set, e.g., X into Z, YY into XX, and YZ into XY. We will calculate only the lowest order term of the average Hamiltonian (*1*),

$$\bar{\mathscr{H}}_{\text{int}}^{0} = \frac{1}{t_{\text{c}}}\int_0^{t_{\text{c}}} \tilde{\mathscr{H}}_{\text{int}}(t')dt', \qquad [11]$$

where t_{c} represents the cycle time of the pulse sequence.

A complication for zero-field multiple-pulse NMR is introduced by different γ_j values of different spin species. At high field, the different resonance frequencies of the various types of spins allow one to excite only one spin species and therefore rotate all affected spins through the same angle. At zero field, a magnetic field pulse of strength B_{p} and duration t_{p} generally affects all the spins in the sample, turning different spin species through different angles ϕ_j:

$$\phi_j = -\gamma_j B_{\text{p}} t_{\text{P}}. \qquad [12]$$

This dependence of the rotation angle on the gyromagnetic ratio of the spin species may be a useful tool for the creation of pulse sequences that act differently on different spin species (*8*).

AVERAGING IN HIGH AND ZERO FIELD

In high magnetic fields it is necessary to take into account only those terms that are invariant with respect to rotation around the z axis, i.e., the Z and ZZ terms, while all other terms are averaged out by the fast precession of the spins around the large magnetic field. The two remaining terms are made time dependent by the application of multiple-pulse sequences. The Carr–Purcell sequence for example is designed to take only the Z term, i.e., chemical shifts and inhomogeneous magnetic fields, into account. By a series of π pulses, the Z term is periodically inverted in the interaction representation $Z, \bar{Z}, Z, \bar{Z}, \ldots$, and thereby averaged to zero. In the case of the WHH-4 sequence, both the Z and the ZZ terms are the objectives of averaging. Their interaction frame values are successively turned along the x, y, and z direction. The ZZ term is therefore averaged to zero while the chemical-shift term Z becomes $(1/3)(X + Y + Z)$.

The toggling-frame transformation of the various terms of the spin Hamiltonian [9] can always be represented as a rotation in three-dimensional space, i.e., by an

element of the three-dimensional rotation group SO(3). We will concentrate here on the case where magnetic field pulses generate rotations by 90° around the coordinate axes. Between the pulses, the transformations [10] are then elements of the cubic rotation group O. The 24 elements of this group generate all possible orientations of a right-handed coordinate system with the axes parallel to one of the original axes as shown in Table 1. We use the shorthand notation $(\alpha\beta\gamma)$ to denote a configuration with $\tilde{X} = \alpha$, $\tilde{Y} = \beta$, and $\tilde{Z} = \gamma$. The principal difference between high-field and zero-field multiple-pulse NMR is that at high field only the value of $\tilde{Z}$ has to be considered while in zero field the full configuration of $\tilde{X}$, $\tilde{Y}$, and $\tilde{Z}$ needs to be accounted for.

TABLE 1

$I_{j\alpha}$ and $I_{j\alpha}I_{k\beta}$ in the 24 Possible Configurations of Right-Handed Coordinate Systems

				$0\times90°$ rotation (E)				
X	Y	Z	XX	YY	ZZ	XX	XZ	YZ
				$1\times90°$ rotation ($6C_4$)				
X	Z	$\bar{Y}$	XX	ZZ	YY	XZ	$-XY$	$-YZ$
X	$\bar{Z}$	Y	XX	ZZ	YY	$-XZ$	XY	$-YZ$
$\bar{Z}$	Y	X	ZZ	YY	XX	$-YZ$	$-XZ$	XY
Z	Y	$\bar{X}$	ZZ	YY	XX	YZ	$-XZ$	$-XY$
Y	$\bar{X}$	Z	YY	XX	ZZ	$-XY$	YZ	$-XZ$
$\bar{Y}$	X	Z	YY	XX	ZZ	$-XY$	$-YZ$	XZ
				$2\times90° = 1\times180°$ ($3C_2$)				
X	$\bar{Y}$	$\bar{Z}$	XX	YY	ZZ	$-XY$	$-XZ$	YZ
$\bar{X}$	Y	$\bar{Z}$	XX	YY	ZZ	$-XY$	XZ	$-YZ$
$\bar{X}$	$\bar{Y}$	Z	XX	YY	ZZ	XY	$-XZ$	$-YZ$
				$2\times90° = 1\times120°$ ($8C_3$)				
Y	Z	X	YY	ZZ	XX	YZ	XY	XZ
Z	X	Y	ZZ	XX	YY	XZ	YZ	XY
$\bar{Y}$	Z	$\bar{X}$	YY	ZZ	XX	$-YZ$	XY	$-XZ$
$\bar{Z}$	$\bar{X}$	Y	ZZ	XX	YY	XZ	$-YZ$	$-XY$
$\bar{Y}$	$\bar{Z}$	X	YY	ZZ	XX	YZ	$-XY$	$-XZ$
Z	$\bar{X}$	$\bar{Y}$	ZZ	XX	YY	$-XZ$	$-YZ$	XY
Y	$\bar{Z}$	$\bar{X}$	YY	ZZ	XX	$-YZ$	$-XY$	XZ
$\bar{Z}$	X	$\bar{Y}$	ZZ	XX	YY	$-XZ$	YZ	$-XY$
				$3\times90° = 180°$ ($6C_2'$)				
$\bar{X}$	$\bar{Z}$	$\bar{Y}$	XX	ZZ	YY	XZ	XY	YZ
$\bar{Z}$	$\bar{Y}$	$\bar{X}$	ZZ	YY	XX	YZ	XZ	XY
$\bar{Y}$	$\bar{X}$	$\bar{Z}$	YY	XX	ZZ	XY	YZ	XZ
Z	$\bar{Y}$	X	ZZ	YY	XX	$-YZ$	XZ	$-XY$
Y	X	$\bar{Z}$	YY	XX	ZZ	XY	$-YZ$	$-XZ$
$\bar{X}$	Z	Y	XX	ZZ	YY	$-XZ$	$-XY$	YZ

The visualization of the rotations that occur during the multiple-pulse experiment can be facilitated by introducing a vector representation for the different terms of the Hamiltonian. The nine basis operators are represented by unit vectors or points on the unit sphere which are rotated by the pulses. Figure 1 shows the nine basis vectors, together with the trajectories they describe under rotations around the coordinate axes. The linear terms correspond exactly to the appropriate unit vectors while XX, YY, and ZZ can be thought of as the same vectors, but points on opposite sides of the sphere are equivalent. The cross terms XY, XZ, and YZ correspond to points halfway between the coordinate axes. Points lying on opposite sides of the sphere are again equivalent.

The trajectories of the linear and quadratic terms correspond to great circles with their axes along the coordinate axes. The cross terms also move along great circles if both components are changed during a transition, i.e., if the rotation axis is orthogonal

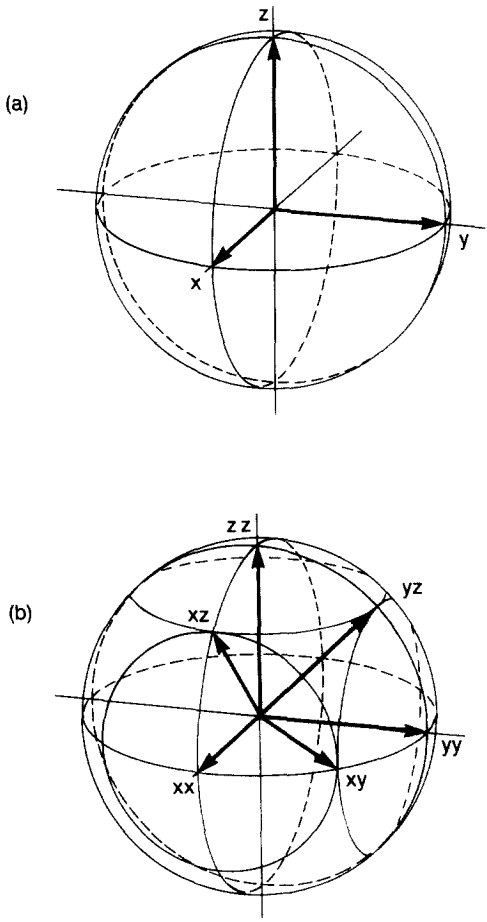

FIG. 1. Vector representation of the basis operators X, Y, and Z (a) and XX, YY, ZZ, XY, XZ, and YZ (b). The circles indicate how the vectors move under rotations around the coordinate axes.

to the direction of the operator. However, if only one component changes, the trajectory follows a circle that intersects the great circles at right angles at the midpoints between coordinate axes.

ZERO-FIELD PULSE SEQUENCES

Sequences of delta-function pulses. If the rotations occur instantaneously, the average Hamiltonian is determined by the toggling-frame Hamiltonians between the pulses. The toggling-frame values of the nine basis operators in the 24 possible configurations are given in Table 1. The zero-order average Hamiltonian of a sequence of delta-function pulses can be calculated by averaging over the configurations that are reached during the pulse sequence. The usual purpose of a multiple-pulse sequence is to average one or several terms of the Hamiltonian to zero.

The linear terms in the Hamiltonian contain the interaction of the spin with the magnetic fields while spin–spin interactions are bilinear. However, if a pulse sequence acts only on one spin species, the heteronuclear couplings to unaffected spins transform like vectors. A sequence that acts only on one spin species I and eliminates the terms that are linear in I from the Hamiltonian while leaving species S unaffected, decouples the I from the S spins. In the high-field case there is only one linear term which can easily be eliminated by a sequence of only two configurations, e.g., (XYZ) and $(X\bar{Y}\bar{Z})$, as in the Carr–Purcell sequence. In the average Hamiltonian of this sequence the Y and Z terms vanish while the X term remains. In zero field, the elimination of only two linear terms would create an anisotropic average Hamiltonian. In general, one needs therefore to eliminate all three linear terms simultaneously. This is not possible in two steps, since the inverse of (XYZ), $(\bar{X}\bar{Y}\bar{Z})$, corresponds to a left-handed coordinate system. A minimum of four configurations is therefore necessary, e.g., (XYZ), $(X\bar{Y}\bar{Z})$, $(\bar{X}\bar{Y}Z)$, and $(\bar{X}Y\bar{Z})$. This sequence of configurations can be traversed by π rotations around the x, y, x and y axes of the toggling frame. Since only π rotations are involved, these directions coincide with the laboratory-frame directions. The pulse sequence

$$(-\pi_x-\pi_y-\pi_x-\pi_y-)_n \qquad [13]$$

with equal delays between the pulses is the zero-field analog of the Carr–Purcell sequence. Note however that it is not possible to generate an echo with this sequence if the cycle time is long compared to the inverse of the size of $\mathscr{H}_{\text{int}}$, since the toggling-frame Hamiltonian does not commute with itself at different times. A laboratory-frame Hamiltonian of $a_xI_x + a_yI_y + a_zI_z$ is converted into $a_xI_x - a_yI_y - a_zI_z$ by the first π rotation which does not commute with the initial value if a_x, a_y, and a_z are independent of each other.

One of the simplest sequences to eliminate the high-field bilinear term ZZ is the WHH-4 sequence. Depending on how the sequence is implemented, it can be viewed as averaging over the configurations (XYZ), $(XZ\bar{Y})$, and $(\bar{Z}YX)$. A sequence that eliminates second-rank interactions at zero field has to eliminate all six bilinear terms simultaneously in order to create an isotropic average Hamiltonian. However, since the transformation properties of the quadratic terms XX, YY, and ZZ differ from those of the cross terms XY, XZ, and YZ, they must be eliminated via different procedures. The quadratic terms XX, YY, and ZZ cannot be inverted but must be averaged

to zero via their isotropic average $XX + YY + ZZ = 0$. This requires a minimum of three configurations such as (XYZ), (YZX), and (ZXY), which can be reached by 120° rotations around the cube body axes or by pairs of 90° rotations around the coordinate axes. Such a sequence eliminates all three quadratic terms simultaneously, in the same number of steps that are required for the single high-field term ZZ. In general, any sequence that averages the quadratic terms to zero must average over a multiple of three configurations.

The cross terms, on the other hand, are eliminated by combining them with their inverse. Since the number of negative cross terms in any given configuration is even, a multiple of four configurations such as (XYZ), $(XZ\bar{Y})$, $(X\bar{Y}\bar{Z})$, and $(X\bar{Z}Y)$ is necessary to eliminate all three cross terms. For the simultaneous elimination of all six bilinear terms it is therefore necessary to use a multiple of 12 configurations. A possible example is the above sequence of four configurations together with their cyclic permutations. The resultant pulse sequence, which can be considered to be the zero-field analog of WHH-4, can be written as

$$(-x-x-x-\bar{z}-y-y-y-\bar{x}-z-z-z-\bar{y}-)_n, \qquad [14]$$

where each letter implies a 90° pulse along the corresponding coordinate axis and equal delays are implied between the pulses. While this sequence contains pulses along all three coordinate axes, it is also possible to achieve the same objective with pulses only along two coordinate axes. The sequence

$$(-x-y-\bar{x}-y-)_{3n} \qquad [15]$$

eliminates all bilinear terms and includes only pulses along the x and y axes. Delta-pulse sequences that eliminate different terms of the Hamiltonian are summarized in Table 2.

Windowless sequences. Since zero-field magnetic resonance is usually performed via indirect detection at high field, it is ideally suited for windowless pulse sequences (*15*), thereby allowing one to reach short cycle times without excessive power requirements. In this case we cannot consider the value of the interaction-frame Hamiltonian

TABLE 2

Summary of δ-Pulse Sequences for Averaging in Zero Field

Term(s) to be eliminated	No. of configurations	Example of configurations
Z	2	(XYZ), $(X\bar{Y}\bar{Z})$
X, Y, Z	4	(XYZ), $(X\bar{Y}\bar{Z})$, $(\bar{X}\bar{Y}Z)$, $(\bar{X}Y\bar{Z})$
ZZ	3	(XYZ), $(XZ\bar{Y})$, $(\bar{Z}YX)$
XX, YY, ZZ	3	(XYZ), (YZX), (ZXY)
XY	2	(XYZ), $(Y\bar{X}Z)$
XY, XZ, YZ	4	(XYZ), $(XZ\bar{Y})$, $(X\bar{Y}\bar{Z})$, $(X\bar{Z}Y)$
All $\alpha\beta$	12	(XYZ), $(XZ\bar{Y})$, $(X\bar{Y}\bar{Z})$, $(X\bar{Z}Y)$ + cyclic permutations
All α, $\alpha\beta$	12	(XYZ), $(\bar{X}\bar{Y}Z)$, $(\bar{X}Y\bar{Z})$, $(X\bar{Y}\bar{Z})$ + cyclic permutations

only between the 90° pulses, but must follow it through the actual rotations. If a linear term is rotated from α to α' during a 90° pulse, its average value is $(2/\pi)(\alpha + \alpha')$. If it stays invariant because it coincides with the rotation axis, its average value is α. Since the two values are incommensurate, it is necessary to consider "stationary points" $\alpha = \alpha'$ separately from the "transitions" with $\alpha \neq \alpha'$. A linear term averages to zero if every stationary point at α is balanced by one at $-\alpha$ and the number of times α appears in a transition is equal to the number of times $-\alpha$ appears. The smallest number of 90° rotations needed to eliminate a single term is four, corresponding to a rotation by 360° along a great circle. It is, however, not necessary for the sequence to contain a multiple of four 90° rotations. The five 90° rotations $Z \rightarrow X \rightarrow Y \rightarrow \bar{X} \rightarrow \bar{Y} \rightarrow \bar{Z}$, for example, create a zero-order average Hamiltonian with vanishing Z term. If all three linear terms are to be eliminated, stationary points are unavoidable. A minimum of sixteen 90° rotations or eight 180° rotations are required to fulfill the above conditions simultaneously for all three terms. A possible pulse sequence is

$$xxyy\ \bar{x}\bar{x}\bar{y}\bar{y}\ \bar{x}\bar{x}\bar{y}\bar{y}\ xxyy. \qquad [16]$$

The resulting trajectories of the relevant terms are represented in Fig. 2 and the corresponding sequence of configurations is given in Table 3.

For the square terms $\alpha\alpha$, a transition $\alpha\alpha \rightarrow \beta\beta$ contributes $1/2(\alpha\alpha + \beta\beta) + 1/\pi\alpha\beta$ to the average Hamiltonian if $\alpha \neq \beta$ and $\alpha\alpha$ if $\alpha = \beta$. The rules to eliminate the high-field bilinear term ZZ (*15*) can be expressed in terms of their trajectories on the unit sphere as follows:

(i) Any trajectory must pass through the points $X = \pm 1$, $Y = \pm 1$, or $Z = \pm 1$ an equal number of times. Stationary points count as two passages.

(ii) Each 90° segment of a great circle must be balanced by an adjacent segment of the same circle.

According to the second rule, the trajectories can always be built up of 180° segments of great circles. Since opposite sides of the unit sphere are equivalent for bilinear terms, 180° segments of great circles play the same role for the bilinear terms as full circles do for linear terms. At least three such segments, one of which may be replaced by

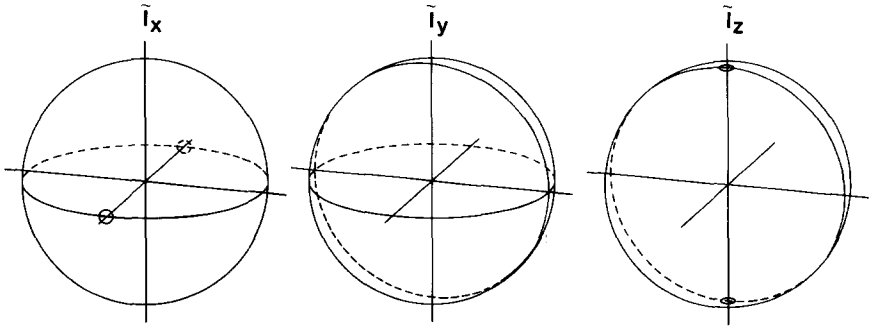

FIG. 2. Trajectories of the three linear terms under the 16-pulse sequence that eliminates them simultaneously. Small circles indicate stationary points.

TABLE 3

Summary of Windowless Sequences for Averaging in Zero Field

Term(s) to be eliminated	No. of 90° rotations	Example
Z	4	$(XYZ) \rightarrow (\bar{Z}YX) \rightarrow (\bar{X}Y\bar{Z}) \rightarrow (ZY\bar{X}) \rightarrow (XYZ)$
X, Y, Z	16	$(XYZ) \rightarrow (XZ\bar{Y}) \rightarrow (X\bar{Y}\bar{Z}) \rightarrow (Z\bar{Y}X) \rightarrow (\bar{X}\bar{Y}Z) \rightarrow (\bar{X}\bar{Z}\bar{Y}) \rightarrow (\bar{X}Y\bar{Z}) \rightarrow (\bar{Z}YX) \rightarrow (XYZ) \rightarrow (X\bar{Z}Y) \rightarrow (X\bar{Y}\bar{Z}) \rightarrow (\bar{Z}\bar{Y}\bar{X}) \rightarrow (\bar{X}\bar{Y}Z) \rightarrow (\bar{X}ZY) \rightarrow (\bar{X}Y\bar{Z}) \rightarrow (ZY\bar{X}) \rightarrow (XYZ)$
ZZ	6	BLEW-6, e.g., $(XYZ) \rightarrow (XZ\bar{Y}) \rightarrow (YZX) \rightarrow (Y\bar{X}Z) \rightarrow (Y\bar{Z}\bar{X}) \rightarrow (\bar{X}\bar{Z}\bar{Y}) \rightarrow (\bar{X}Y\bar{Z})$
XX, YY, ZZ	6	$(XYZ) \rightarrow (XZ\bar{Y}) \rightarrow (YZX) \rightarrow (Z\bar{Y}X) \rightarrow (ZXY) \rightarrow (\bar{Y}XZ) \rightarrow (XYZ)$
XY	2	$(XYZ) \rightarrow (Y\bar{X}Z) \rightarrow (\bar{X}\bar{Y}Z)$
XY, XZ, YZ	4	$(XYZ) \rightarrow (XZ\bar{Y}) \rightarrow (X\bar{Y}\bar{Z}) \rightarrow (XYZ)$
All $\alpha\beta$	24	$(XYZ) \rightarrow (XZ\bar{Y}) \rightarrow (\bar{Y}Z\bar{X}) \rightarrow (\bar{Y}XZ) \rightarrow (ZXY) \rightarrow (ZY\bar{X}) \rightarrow (\bar{X}Y\bar{Z}) \rightarrow (\bar{X}ZY) \rightarrow (YZX) \rightarrow (YX\bar{Z}) \rightarrow (\bar{Z}XY) \rightarrow (\bar{Z}YX) \rightarrow (XYZ) \rightarrow (X\bar{Z}Y) \rightarrow (Y\bar{Z}\bar{X}) \rightarrow (YX\bar{Z}) \rightarrow (ZXY) \rightarrow (Z\bar{Y}X) \rightarrow (X\bar{Y}\bar{Z}) \rightarrow (XZ\bar{Y}) \rightarrow (YZX) \rightarrow (Y\bar{X}Z) \rightarrow (Z\bar{X}\bar{Y}) \rightarrow (ZY\bar{X}) \rightarrow (XYZ)$

two stationary points, are required to eliminate ZZ. Apart from rotations around the z axis there is only one possible way to arrange three semicircles without violating rule (i). The resulting trajectory, corresponding to a BLEW-6 sequence, is shown in Fig. 3. These rules can equally be applied for the elimination of the terms XX and

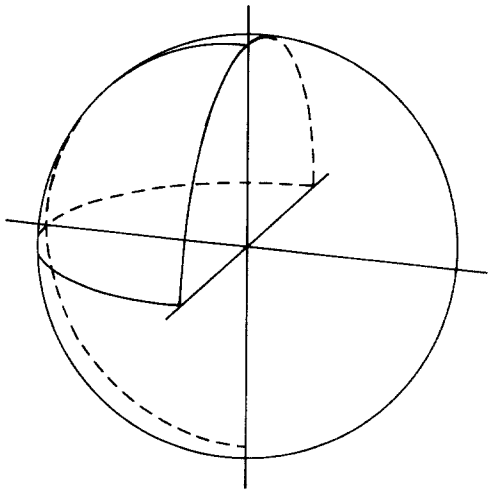

FIG. 3. Trajectory of ZZ under a BLEW-6 sequence.

YY. With the same number of six 90° rotations it is possible to average all three terms to zero, e.g., with the pulse sequence

$$(xyz)_{2n}. \qquad [17]$$

Figure 4 shows the resulting trajectory which is the same for all three terms. Note that the trajectory includes two stationary points (small circles).

The cross terms again behave differently. We must distinguish "semistationary transitions" such as $\alpha\beta \rightarrow \alpha\beta'$ which contribute $2/\pi(\alpha\beta + \alpha\beta')$ to the average Hamiltonian from inverting transitions $\alpha\beta \rightarrow \alpha'\beta' = -\beta\alpha$ which add $\pm 1/\pi(\alpha\alpha - \beta\beta)$. In terms of trajectories on the unit sphere, inverting transitions correspond to segments of great circles and must be balanced by adjacent segments of the same great circle for the corresponding term to vanish. Thus again 180° segments of great circles in the trajectories of the cross terms are analogous to full circles for linear terms. The semistationary transitions do not correspond to great circles, since the operators are not orthogonal to the rotation axis, but intersect them at right angles at the midpoints between coordinate axes (see Fig. 1). Their contributions to the average Hamiltonian vanish if the number of occurrences of $\alpha\beta$ is equal to the number of occurrences of $-\alpha\beta$. A trajectory $\alpha\beta \rightarrow \alpha\beta'$ must therefore be balanced by one from $-\alpha\beta$ to $-\alpha\beta'$ which lies on the opposite side of the same circle, up to an inversion at the origin. A single cross term can be eliminated by two successive inversions $\alpha\beta \rightarrow -\beta\alpha \rightarrow \alpha\beta$. If all three terms are to be eliminated simultaneously, semistationary trajectories are unavoidable. Therefore, a minimum of four 90° rotations is necessary in this case, combined into one 360° rotation. All bilinear terms can be eliminated with a sequence of twenty-four 90° rotations. An example of such a sequence is

$$(x\bar{y}\bar{x}\bar{y})_3(\bar{x}\bar{y}\bar{x}y)_3. \qquad [18]$$

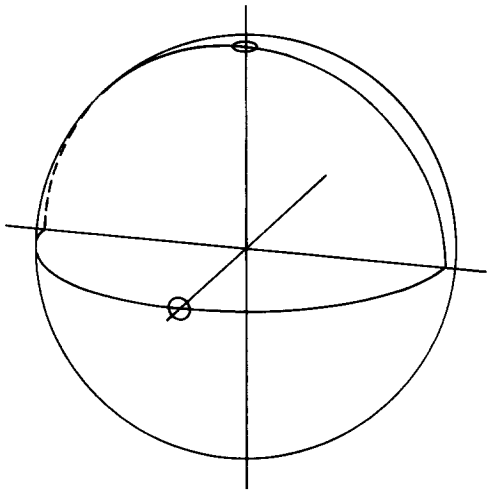

FIG. 4. Trajectory of *XX*, *YY*, and *ZZ* under the windowless six-pulse sequence that eliminates them simultaneously. All three terms follow the same trajectory.

Table 3 summarizes the number of 90° rotations that eliminate different terms of the Hamiltonian.

Isotropic chemical shift. Instead of averaging the linear terms to zero, it is equally possible to average them to a nonvanishing isotropic value. At high fields, isotropic chemical shifts are usually observed by rapid spinning of the sample around an axis tilted by the magic angle $\Theta_m = 54.7°$ with respect to the static magnetic field. As an alternative, it is also possible to keep the sample fixed and move the magnetic field around a suitable trajectory. The chemical shift becomes truncated with respect to the instantaneous direction of the precessing magnetic field. It thus becomes time dependent and can be averaged to its isotropic value by choosing an appropriate trajectory for the magnetic field. Two possible experiments are shown in Fig. 5. In experiment a, a magnetic field is rotated at the magic angle around the laboratory z axis. Experiment b is a "sudden" version, corresponding to magic-angle hopping, that samples three mutually orthogonal space directions. The pulses between the "static" magnetic fields rotate the spins to follow the changing direction of the magnetic field. Both experiments not only eliminate the chemical-shift anisotropy, but also average dipolar and quadrupolar interactions to their isotropic value, i.e., to zero. The averaging of the interactions occurs in two steps. First, they are truncated with respect to the instantaneous direction of the magnetic field. On a time scale slow compared to the Larmor frequency, the magnetic field is then moved to sample at least three orthogonal directions in space.

If isotropic chemical shifts are to be observed at low magnetic fields, it is possible to eliminate second-rank interactions with a multiple-pulse sequence that leads to a nonvanishing linear term in the average Hamiltonian which can be made isotropic by cyclically permuting the direction of the pulses and the external field. Using the pulse sequence

$$(z\bar{x}\bar{z}\bar{x})_{3n}, \qquad [19]$$

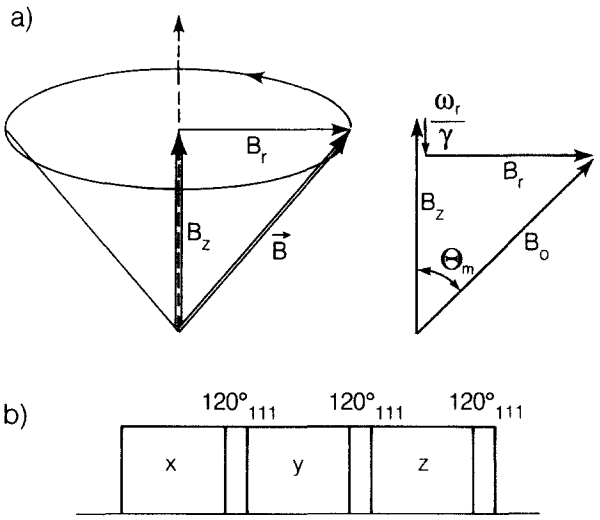

FIG. 5. Two experiments that recover isotropic chemical shifts from a static sample.

one must apply the "static" magnetic fields B_0 in the following directions:

$$\begin{array}{ll} B_0 & x \quad y \quad z \\ B_P & (z\bar{x}\bar{z}\bar{x})_3(x\bar{y}\bar{x}\bar{y})_3(y\bar{z}\bar{y}\bar{z})_3. \end{array} \quad [20]$$

In the limit of delta-function pulses, this sequence creates the desired average Hamiltonian

$$\bar{\mathscr{H}}^{(0)} = 1/3(a_x + a_y + a_z)(I_x + I_y + I_z), \quad [21]$$

while the bilinear terms vanish. With $\mathscr{H}_1$ as given in Eq. [1] we find

$$\bar{\mathscr{H}}^{(0)} = -\gamma B_0(1-\sigma)1/3(I_x + I_y + I_z), \quad [22]$$

where B_0 represents the strength of the magnetic field which is applied sequentially along the x, y, and z direction of the laboratory frame of reference. $\sigma = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$ represents the isotropic chemical shift. The sequence may also be used in the windowless limit. The resulting average Hamiltonian then becomes

$$\bar{\mathscr{H}}^{(0)} = -\gamma B_0(1-\sigma)(1+4/\pi)/6(I_x + I_y + I_z), \quad [23]$$

with a slightly bigger scaling factor.

Relationship to iterative pulse schemes at high field. Iterative schemes to generate pulse sequences have come into use mainly in the context of composite pulses and spin decoupling (*16, 17*). In such a procedure, an initial pulse sequence is changed by shifting the phase of the whole sequence and permuting parts of the sequence from one end to the other. A phase shift ϕ rotates the average Hamiltonian $\bar{\mathscr{H}}$ of the original sequence into

$$\bar{\mathscr{H}}' = e^{-i\phi I_z}\bar{\mathscr{H}}e^{i\phi I_z}. \quad [24]$$

If the element that is permuted generates a propagator U_P and is permuted from right to left, the new sequence has an average Hamiltonian

$$\bar{\mathscr{H}}' = U_P\bar{\mathscr{H}}U_P^{\dagger}. \quad [25]$$

The altered sequences are then combined into a new, longer sequence such that the overall average Hamiltonian corresponds more closely to the desired one. The extended sequence is then used again as the next seed for the recursive expansion procedure.

The average Hamiltonian of a pulse sequence can in general contain all the terms of the low-field Hamiltonian, Eq. [1]. The average Hamiltonian $\bar{\mathscr{H}}$ can therefore be considered to describe a spin system in a low magnetic field and the effect of the phase shifts and permutations are analogous to magnetic field pulses applied to that system.

A well-known expansion scheme is MLEV. As shown in Fig. 6, it includes the two steps of permuting a 180° pulse of the original sequence (Fig. 6b) and combining the original and the permuted sequences with their phase-shifted images to form a new sequence (Fig. 6c). The individual cycles have the average Hamiltonians

$$\bar{\mathscr{H}},\ e^{-i\pi I_x}\bar{\mathscr{H}}e^{i\pi I_x},\ e^{-i\pi I_x}e^{-i\pi I_z}\bar{\mathscr{H}}e^{i\pi I_z}e^{i\pi I_x},\ e^{-i\pi I_z}\bar{\mathscr{H}}e^{i\pi I_z}. \quad [26]$$

The same terms are obtained if the analog of the Carr–Purcell sequence, $(-\pi_x-\pi_z-\pi_x-\pi_z-)_n$, is applied to a low-field Hamiltonian. The error terms occurring in high-field pulse sequences contain in general all the terms of the low-field Hamiltonian and

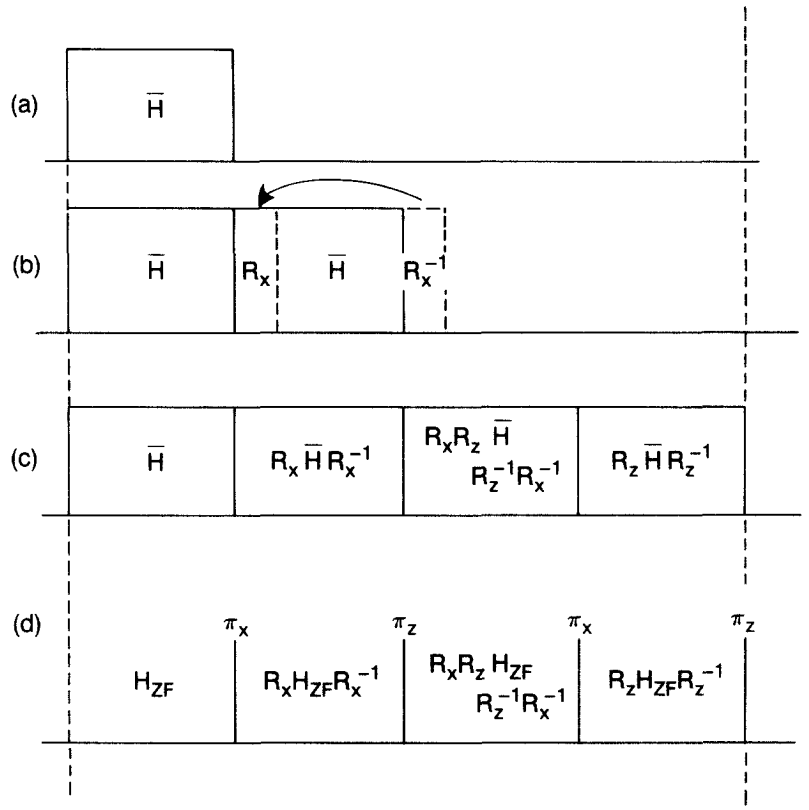

FIG. 6. Correspondence between the MLEV recursive expansion scheme (a)–(c) and the zero-field analog of the Carr–Purcell sequence (d).

the MLEV scheme is designed to remove all three linear terms, thereby ensuring good decoupling. Other iterative schemes that have been conceived to eliminate linear and bilinear terms (*14*) also correspond to zero-field pulse sequences.

CONCLUSIONS

It is possible to develop pulse sequences that selectively average out certain terms of the full low-field spin Hamiltonian. The resulting pulse sequences tend to be longer than the corresponding pulse sequences at high magnetic field because they have to cancel a larger number of terms. The duality between spatial rotations of the sample and rotation of the spins generated by magnetic fields provide important insight into zero- as well as high-field experiments and suggests possible alternatives to existing experiments using sample reorientation. Information about the transformation properties and the possible ways to eliminate the terms of the zero-field Hamiltonian is also important in high-field experiments where these terms appear as imperfections.

One problem not covered in this article is that in zero field it is not possible to distinguish the different spin species present in the sample by their resonance frequency. A single magnetic field pulse therefore affects in general all the spins present in the

sample, rotating them through different angles determined by the gyromagnetic ratios. Several possibilities can be envisaged for the design of experiments that act selectively on only one spin species. One is to capitalize on certain special values of gyromagnetic ratios. Thus it has been shown (*8*) that it is possible to apply pulses that act like 2π pulses on protons and as $\pi/2$ pulses on ^{13}C. In the limit of ideal delta-function pulses, such a pulse affects only the ^{13}C system and can thus be used for selective experiments in heteronuclear systems. Another possibility is the use of bistable excitation sequences (*18*) that generate a composite pulse which acts as a perfect pulse for a certain range of gyromagnetic ratios and leaves spins with other γ values unaffected.

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