Pages 2-33 of this pdf file are Tycko's lecture slides from January 8, 2018. Pages 34-74 are notes about quantum mechanics, NMR, homonuclear recoupling, and related things, prepared originally in 2008 and subsequently corrected/amended.
Introduction to the (Quantum Mechanical) Theory of Solid State NMR

1. How do we describe the state of a nuclear spin system?
2. Angular momentum and rotations
3. How do we represent the interactions of nuclear spins that determine NMR signals?
4. How do we calculate NMR signals?
5. Nuclear spin interactions that affect solid state NMR (dependence on structure, orientation, motion)
6. Manipulation of spin interactions by radio-frequency pulses and sample spinning (Average Hamiltonian theory; recoupling)

(R. Tycko, 2018 Winter School on Biomolecular Solid State NMR)
How do we describe the state of a nuclear spin system?

In quantum mechanics, the state of a system at time $t$ can be represented by the abstract symbol $|\psi(t)\rangle$, which is called a state vector.

State vectors have "complex conjugates", which are written as $\langle\psi(t)|$.

State vectors have a "length", defined as the inner product $\langle\psi(t)|\psi(t)\rangle$.

The inner product $\langle\phi|\psi\rangle$ represents the projection of one state vector onto another state vector. If $\langle\phi|\psi\rangle = 0$, the two states are orthogonal to one another. Note that $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$.

For any system, there is a set of states that represents all possible conditions of the system. Such a set is called a basis. (In fact, there are many different bases for a given system.)

For a spin-1/2 nucleus (e.g., 1H, 13C, 15N, 31P), the basis can be $\{|+\rangle,|−\rangle\}$. In other words, the two states in which the spin is either "pointing up" or "pointing down".

This means that any state of the spin-1/2 nucleus is some linear combination of $|+\rangle$ and $|−\rangle$. In other words, $|\psi(t)\rangle = a(t)|+\rangle + b(t)|−\rangle$, where $a(t)$ and $b(t)$ are complex numbers.

The basis states are usually chosen to be "orthonormal", meaning that $\langle+|+\rangle = \langle−|−\rangle = 1$ and $\langle+|−\rangle = 0$. Also, $|a|^2 + |b|^2 = 1$, so that $\langle\psi(t)|\psi(t)\rangle = 1$. 

How do we describe the state of a nuclear spin system?

For a many-spin system, we can choose the basis to be \( \{ |m_1 m_2 m_3 \ldots m_N \rangle \} \), where \( m_j \) is the "direction" of the \( j^{\text{th}} \) spin. If all of the nuclei are spin-1/2, the basis contains \( 2^N \) state vectors. This choice of basis is called the "direct product" basis.

The overall state of the many-spin system can then be written as

\[
|\psi(t)\rangle = \sum_{m_1, m_2, \ldots, m_N = -s}^{+s} a_{m_1, m_2, \ldots, m_N}(t) |m_1 m_2 \ldots m_N \rangle
\]

In standard quantum mechanics, the squared magnitudes of the coefficients in such a linear combination represent the probabilities of being in each individual state. If you were to ask for the probability that the many-spin system at time \( t \) was in the state where \( m_1 = +1/2, m_2 = +1/2, m_3 = -1/2, m_4 = -1/2, \) etc., the answer would be \( |a_{+,+,+,\ldots}|^2 \).

The relative phases of the coefficients are also important. For example, in a one-spin system, the states \( |\psi_1\rangle = a|+\rangle + b|-\rangle \) and \( |\psi_2\rangle = a|+\rangle + ib|-\rangle \) are different. If \( a = b = 2^{-1/2} \), then \( |\psi_1\rangle \) is a state that "points" along +x, while \( |\psi_2\rangle \) is a state that "points" along +y.

The description given so far applies when all of the coefficients have precisely defined magnitudes and phases, so that there is a unique linear combination of basis states that fully describes the overall state of the spin system. Such a state is called a "pure state".

This may happen in other areas of science, but it does not happen in NMR.
How do we describe the state of a nuclear spin system?

What happens in NMR is that we have many copies of nominally identical spin systems, all of which contribute simultaneously to our NMR signals, but each of which is in a different quantum mechanical state. The "many copies" could be the individual molecules within our sample, or they could be different nanometer-scale pieces within a larger chunk of material.

The different copies have different values of their complex coefficients in the linear combination of basis states on the previous slide.

If we knew the probability of having each specific choice of complex coefficients, then we could calculate NMR signals from each specific choice, and add up the results from many, many such calculations to get the total NMR signal. This would be perfectly correct, but it would be very inconvenient and laborious.

A more convenient, concise, and tractable approach is to use a density operator (or density matrix) description of the state of the nuclear spin system.

The density operator approach allows us to average over the many copies of identical spin systems. But it is not the same as simply taking the average quantum mechanical state.

\[
\left| \psi(t) \right\rangle = \sum_{m_1,m_2,\ldots,m_N=-s}^{+s} a_{m_1,m_2,\ldots,m_N}(t) \left| m_1m_2\ldots m_N \right\rangle = \sum_{m_1,m_2,\ldots,m_N=-s}^{+s} a_{m_1,m_2,\ldots,m_N}(t) \left| m_1m_2\ldots m_N \right\rangle
\]

\[
\rightarrow \sum_{m_1,m_2,\ldots,m_N=-s}^{+s} b_{m_1,m_2,\ldots,m_N}(t) \left| m_1m_2\ldots m_N \right\rangle \quad \text{This is still a pure state.}
\]
Digression: what is an operator?

An operator $O$ is something that transforms a state $|\psi\rangle$ to another state $|\psi'\rangle$, written as the equation $O|\psi\rangle = |\psi'\rangle$. In quantum mechanics and NMR, we are mostly concerned with linear operators, which have the property that $O(a|\psi\rangle + b|\phi\rangle) = aO|\psi\rangle + bO|\phi\rangle = |\psi'\rangle + |\phi'\rangle$.

Some, but not all, operators have inverses, represented by $O^{-1}$, such that $OO^{-1} = O^{-1}O = 1$. Here, the symbol "1" means the "identity operator", which has the property that $1|\psi\rangle = |\psi\rangle$ for any state $|\psi\rangle$.

Some operators have "eigenstates", which are special states that are transformed into themselves, multiplied by a number $\lambda$ that is called the "eigenvalue". So for an eigenstate of $O$, $O|\phi\rangle = \lambda|\phi\rangle$. In general, $\lambda$ is a complex number.

All linear operators have "adjoints", symbolized by $O^\dagger$. Adjoint operators are like complex conjugates. If $O|\psi\rangle = |\psi'\rangle$, then $\langle\psi|O^\dagger = \langle\psi'|$. And $(cO)^\dagger = c^*O^\dagger$.

Two different operators usually do not commute with one another, meaning that $O_1O_2 \neq O_2O_1$. The operator $[O_1,O_2] \equiv O_1O_2 - O_2O_1$ is called the "commutator of $O_1$ with $O_2$".

If two operators do commute, then they have the same eigenstates (unless there are "degenerate" eigenstates, i.e., groups of eigenstates with the same eigenvalue).

If two operators have the same eigenstates, then they commute (when operating on their eigenstates).
Digression: what is an operator?

In quantum mechanics and NMR, we are particularly interested in two special types of linear operators, namely "Hermitian" operators and "unitary" operators.

Hermitian operators have a **complete set of eigenstates**, so that the eigenstates can be used as a **basis** to represent any other state of the system. In other words, any state can be written as a linear combination of the eigenstates. Moreover, the **eigenvalues are real numbers**. Consequently, if A is Hermitian, then $A^\dagger = A$. A is called "self-adjoint".

Hermitian operators are used to describe energies (i.e., terms in the nuclear spin Hamiltonian) and other observable quantities (e.g., angular momentum components). The fact that Hermitian operators have real eigenvalues implies that observable quantities are real numbers.

Unitary operators have the property that their adjoints are their inverses. In other words, if B is unitary, then $B^\dagger = B^{-1}$. And vice versa. Consequently, unitary operators **preserve inner products** of pairs of states. If $B|\psi\rangle = |\psi'\rangle$ and $B|\phi\rangle = |\phi'\rangle$, then $\langle \phi'|\psi'\rangle = \langle \phi|\psi\rangle$.

Unitary operators are used to describe the evolution in time of a quantum mechanical state, as in $|\psi(t)\rangle = U(t)|\psi(0)\rangle$, where $U(t)$ is the "time evolution operator".

Unitary operators are also used to describe rotations and similar transformations. So quantum mechanically, an rf pulse is a unitary operator.
Digression: matrices and vectors

Sometimes we can calculate NMR signals by using the abstract symbols for operators and states discussed so far. More frequently, signals are calculated in computer programs by using matrices and vectors.

Converting the abstract symbols to matrices and vectors requires us to choose a specific basis set, for example the direct product basis \( \{ |m_1m_2m_3...m_N \rangle \} \).

If the basis states are written simply as \(|k\rangle\), with \(k = 1,2,...,N\):

A state \( |\psi\rangle = \sum_{k=1}^{N} a_k |k\rangle \) is represented by an N-dimensional column vector, with elements \(a_k\).

\( \langle \psi | \) is represented by an N-dimensional row vector, with elements \(a_k^*\).

An operator \( O \) is represented by an \( N \times N \) matrix, with the number \( \langle j | O | k \rangle \) in row \( j \) and column \( k \).

A Hermitian matrix has real numbers along the diagonal (\(j = k\)). Off-diagonal elements on opposite sides of the diagonal are complex conjugates of one another, because \( \langle j | O | k \rangle = \langle k | O | j \rangle^* \) for a Hermitian operator.

For a unitary matrix, rows and columns are orthonormal:

\[
\sum_{k=1}^{N} O_{qk} O_{rk}^* = \sum_{k=1}^{N} \langle q | O | k \rangle \langle r | O | k \rangle^* = \sum_{k=1}^{N} \langle q | O | k \rangle \langle k | O^\dagger | r \rangle = \langle q | O O^\dagger | r \rangle = \langle q | O O^{-1} | r \rangle = \langle q | r \rangle = \delta_{q,r}
\]

\[
\sum_{k=1}^{N} O_{kq} O_{kr}^* = \sum_{k=1}^{N} \langle k | O | q \rangle \langle k | O | r \rangle^* = \sum_{k=1}^{N} \langle k | O | q \rangle \langle r | O^\dagger | k \rangle = \sum_{k=1}^{N} \langle r | O^\dagger | k \rangle \langle k | O | q \rangle = \langle r | O^\dagger O | q \rangle = \langle r | q \rangle = \delta_{r,q}
\]
How do we describe the state of a nuclear spin system?

Now back to the density operator as a description of a "mixed state" in NMR, *i.e.*, a sample that contains many copies of the same spin system, each in a different quantum mechanical state, and all contributing simultaneously to the NMR signals:

The density operator \( \rho(t) \) is defined to be the average of \( |\psi(t)\rangle\langle \psi(t)| \), where \( |a\rangle\langle b| \) is the outer product of states \( |a\rangle \) and \( |b\rangle \).

\[
\rho(t) = \langle \psi(t) | \psi(t) \rangle
\]

An outer product of two states is an operator, because it can be applied to some other state according to \( (|a\rangle\langle b|)|\phi\rangle = |a\rangle\langle b|\phi\rangle = x|a\rangle \), with \( x = \langle b|\phi\rangle \). Such operators are sometimes called "projection operators".

If we express the state in a basis \( \{|k\rangle\} \) as \( |\psi(t)\rangle = \sum_{k=1}^{N} a_k(t) |k\rangle \), then the density operator is

\[
\rho(t) = \sum_{k=1}^{N} a_k(t) |k\rangle \sum_{k'=1}^{N} a_{k'}(t)^* \langle k'| = \sum_{k=1}^{N} \sum_{k'=1}^{N} a_k(t) a_{k'}(t)^* |k\rangle \langle k'|
\]

In this basis, the density matrix has the number \( \rho_{kk'}(t) = a_k(t)a_{k'}(t)^* \) in row \( k \) and column \( k' \).

Diagonal elements of the density matrix (\( k=k' \)) are the population of state \( |k\rangle \), in other words the overall probability of finding the system in this state, averaged over the "many copies".

Off-diagonal elements (\( k\neq k' \)) are called "coherences". A non-zero coherence means that there is a non-random relationship between the amplitudes of states \( |k\rangle \) and \( |k'\rangle \).
How do we describe the state of a nuclear spin system?

The density operator sounds complicated, but actually it makes calculations of signals relatively simple, especially when the initial "mixed state" of the system is something simple.

If the system has quantum mechanical energy levels \( E_k \) \((k = 1, 2, ..., N)\) and if the system is initially at thermal equilibrium, then the relative populations of the energy levels are given by Boltzmann factors, so \( \rho_{kk}(0) \propto \exp(-\beta E_k) \), where \( \beta = 1/k_B T \). At thermal equilibrium, coherences between different energy states are assumed to be zero, so \( \rho_{kk'}(0) = 0 \) for \( k \neq k' \).

In general, if the Hamiltonian of the system \((i.e., \) the energy operator\) is \( H \), then at thermal equilibrium, \( \rho(0) \propto \exp(-\beta H) \). The density matrix elements then have these properties.

In a high-field NMR experiment, the largest part of the Hamiltonian is the Zeeman interaction with the large external field along \( z \). For a homonuclear system with NMR frequency \( \omega_0 \), this is \( H_Z = \omega_0 S_z \), where \( S_z \) is the \( z \)-component of spin angular momentum. It is therefore a very good approximation to use \( \rho(0) \propto \exp(-\beta H_Z) = \exp(-\beta \omega_0 S_z) \).

It is also true that \( \beta \omega_0 \ll 1 \), except at very, very low temperatures. Therefore, \( \rho(0) \propto 1 - \beta \omega_0 S_z \).

The "1" does not contribute to NMR signals. So in signal calculations, we can say \( \rho(0) \propto S_z \).

This corresponds to an initial state with the nuclear spins weakly polarized along the external field.
The "spin" of a nucleus is the total angular momentum of the nucleus (in its ground state).

Angular momentum in quantum mechanics is represented by operators such as $S_x$, $S_y$, and $S_z$. These are the x, y, and z components of the angular momentum vector operator $\mathbf{S}$.

Angular momentum components do not commute with one another, which means that spin states can be eigenstates of only one angular momentum component, most commonly $S_z$.

The commutators are $[S_x,S_y] = iS_z$ and $[S_y,S_z] = iS_x$ and $[S_z,S_x] = iS_y$ (with Planck's constant $\hbar$ = 1).

These commutation relations dictate the properties of angular momentum operators, and any other set of operators with the same commutation relations will behave in the same way as angular momentum operators.

Each angular momentum component does commute with $S^2 = S_x^2 + S_y^2 + S_z^2$. So NMR-active nuclei have a quantum number $s$, which defines the eigenvalue of $S^2$ to be $s(s+1)$, and they can simultaneously have eigenvalues of $S_z$, ranging from $-s$ to $+s$ in increments of 1.

This can be proven from the commutation relations. It is convenient to define spin "raising" and "lowering" operators $S_+ = S_x + iS_y$ and $S_- = S_x - iS_y$. If $|m\rangle$ is an eigenstate of $S_z$ with eigenvalue $m$ (i.e., $S_z|m\rangle = m| m\rangle$), then $S_+|m\rangle$ and $S_-|m\rangle$ are eigenstates of $S_z$ with eigenvalues $m+1$ and $m-1$.

Except that, if $m = s$, then $S_+|m\rangle = 0$. And if $m = -s$, then $S_-|m\rangle = 0$. 
Angular momentum and rotations

In general:  \( S_+ |m\rangle = \sqrt{s(s+1) - m(m+1)} |m+1\rangle \) and  \( S_- |m\rangle = \sqrt{s(s+1) - m(m-1)} |m-1\rangle \)

These relations tells us the matrix elements of \( S_+ \) and \( S_- \). In the basis \( |m\rangle \), diagonal elements are zero. The only non-zero elements are one space off the diagonal.

Using \( S_x = (S_+ + S_-)/2 \) and \( S_y = (S_+ - S_-)/2i \), we can then construct matrices for \( S_x \) and \( S_y \).

For a spin-1/2 nucleus, the "Pauli spin matrices" are:

\[
S_x = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \quad S_y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \quad S_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}
\]

\[1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\]

For a pair of spin-1/2 nuclei, \( S_x = S_{x1} + S_{x2} \), \( S_y = S_{y1} + S_{y2} \), and \( S_z = S_{z1} + S_{z2} \). How can we write these as matrices in the 4-dimensional direct-product basis \( \{|++\rangle, |+-\rangle, |--\rangle, |--\rangle\} \)?

We can think of such things as \( S_x = S_{x1} \otimes 1_2 + 1_1 \otimes S_{x2} \), where the "tensor product" \( \otimes \) means:

\[
\begin{pmatrix} a & b \\ c & d \end{pmatrix} \otimes \begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} aA & bA & aB & bB \\ cA & dA & cB & dB \\ aC & bC & aD & bD \\ cC & dC & cD & dD \end{pmatrix}
\]

In this way, matrices for \( S_x, S_y, \) and \( S_z \) can be constructed for arbitrarily large spin systems, for example in an NMR simulation program.
Angular momentum operators are "generators" of rotations. This means that the unitary operator $R(\alpha) = \exp(-iS \cdot \alpha)$ is a rotation operator. Specifically, $R(\alpha)$ rotates angular momenta around an axis given by the direction of the vector $\alpha$, by a rotation angle given by the magnitude of $\alpha$.

For example, $R_x(\theta) = \exp(-iS_x \theta)$ is a rotation around $x$ by $\theta$. We apply this rotation to states according to $|\psi'\rangle = R_x(\theta)|\psi\rangle$.

We apply this rotation to operators according to $O' = R_x(\theta)OR_x(\theta)^{-1} = R_x(\theta)OR_x(-\theta)$. It can be shown that: 

$$R_x(\theta)S_yR_x(-\theta) = e^{-iS_x \theta}S_y e^{iS_x \theta} = S_y \cos \theta + S_z \sin \theta$$

and similar relations for rotations around $y$ and $z$. This is what one expects for rotations in a right-handed axis system. These relations can be proven (laboriously) by expanding $\exp(-iS_x \theta)$ and $\exp(iS_x \theta)$ in Taylor series and using the commutation relations to rearrange the resulting expressions.
A few interesting facts about rotations:

--Any product of rotation operators is equivalent to a single rotation operator for some vector $\alpha$. In other words, there is always some net rotation axis and net rotation angle.

--Any rotation or product of rotations can be expressed as $R_z(\alpha)R_y(\beta)R_z(\gamma)$ for some choice of "Euler angles" $\alpha, \beta, \gamma$.

--Products of rotation operators can often by simplified or rearranged by tricks such as the following:

$$R_x(\pi/2)R_z(\pi/2)R_y(\pi/2)R_z(\pi/2) = R_x(\pi/2)R_z(\pi/2)R_y(\pi/2)R_z(-\pi/2)R_z(\pi/2)$$

$$= R_x(\pi/2)R_z(\pi/2)R_y(\pi/2)R_z(-\pi/2)R_z(\pi/2)$$

$$= R_x(\pi/2)R_x(-\pi/2)R_z(\pi/2)R_z(\pi/2)$$

$$= R_z(\pi)$$

The third line follows from the second line because of the general relation, for any unitary operator $U$ and any operator $A$, that

$$Ue^A U^{-1} = e^{UAU^{-1}}$$

This is proven easily by expanding $e^A$ as a Taylor series.

In fact, for any function $F$, $UF(A)U^{-1} = F(UAU^{-1})$. 
How do we represent the interactions that determine NMR signals?

Interactions of nuclear spins with one another, with external fields, and with their chemical/material environment are represented by the Hamiltonian operator $H(t)$, which is a Hermitian operator. The eigenvalues of $H(t)$ are the instantaneous energy levels of the spin system. Because $H(t)$ is Hermitian, it always has a complete set of eigenstates, which could therefore be used as a basis.

The Hamiltonian generally is a sum of terms, each representing one type of interaction. In high-field NMR, the largest term is the Zeeman interaction with the external magnetic field along $z$, $H_Z = \omega_0 S_z$, where $\omega_0$ is the Larmor frequency in radians per second (again assuming Planck's constant $\hbar = 1$, so that energies are measured in rad/s).

(If there are two different types of spins, called $S$ and $I$ for example, then $H_Z = \omega_0 S_z + \omega_0 I_z$.)

Interactions of spins with rf pulses are represented (in the laboratory frame) by terms of the form $H_{\text{rf}}(t) = 2\omega_1 \cos(\omega_{\text{rf}} t - \phi) S_x$, where $\omega_1$ is the rf amplitude, $\phi$ is the rf phase, and $\omega_{\text{rf}}$ is the rf frequency, or "carrier frequency". In the rotating frame, $H_{\text{rf}} = \omega_1 (S_x \cos \phi + S_y \sin \phi)$ as will be shown later.

Other terms, such as terms representing spin-spin couplings, are contained in an "internal Hamiltonian" $H_{\text{int}}(t)$, with a time-dependence that may arise from sample spinning or molecular motions. Details of these terms will be discussed later.

So usually the Hamiltonian can be written as $H(t) = H_Z + H_{\text{rf}}(t) + H_{\text{int}}(t)$.
How do we represent the interactions that determine NMR signals?

The Hamiltonian determines how the state of the system changes with time. In other words, the Hamiltonian is the generator of time evolution, just as angular momentum operators are generators of rotations.

Time evolution is described by a unitary time-evolution operator $U(t)$, which transforms states according to $|\psi(t)\rangle = U(t)|\psi(0)\rangle$ and transforms density operators according to $ho(t) = U(t)\rho(0)U(t)^{-1}$.

The Schrödinger equation of standard quantum mechanics says

$$i \frac{d}{dt} |\psi(t)\rangle = H(t)|\psi(t)\rangle$$

If $|\psi(t)\rangle = U(t)|\psi(0)\rangle$ for any initial state $|\psi(0)\rangle$, then it must be true that

$$i \frac{d}{dt} U(t) = H(t)U(t)$$

This is the Schrödinger equation for $U(t)$. In the special case that $H(t) = H_0$ for all $t$, the solution is $U(t) = \exp(-iH_0 t)$.

If $H(t)$ is "piecewise constant", equal to $H_0$, $H_1$, ..., $H_M$ for successive time periods of length $t_0$, $t_1$, ..., $t_M$, then the overall evolution operator up to time $\tau = t_0 + t_1 + ... + t_M$ is

$$U(\tau) = \exp(-iH_M t_M) ... \exp(-iH_1 t_1) \exp(-iH_0 t_0)$$

Note that the order of terms in this product is very important, because in general $[H_p, H_q] \neq 0$.

And note that the inverse evolution operator (for going backwards in time) has the opposite order: $U(\tau)^{-1} = \exp(iH_0 t_0) \exp(iH_1 t_1) ... \exp(iH_M t_M)$.
How do we represent the interactions that determine NMR signals?

In the special case that the Hamiltonian does commute with itself at different times, it is OK to add the exponents: $U(\tau) = \exp[-i(H_M t_M +...+ H_1 t_1 + H_0 t_0)]$ and $U(\tau)^{-1} = \exp[i(H_M t_M +...+ H_1 t_1 + H_0 t_0)]$

If $H(t)$ is a general function of time, not necessarily piecewise-constant, and $[H(t),H(t')] = 0$ for any two times $t$ and $t'$, this becomes $U(t) = \exp[-i\int_0^t H(t')dt']$ and $U(t)^{-1} = \exp[i\int_0^t H(t')dt']$

If $H(t)$ is a general function of time and $[H(t),H(t')] \neq 0$, we can write $U(t) = \bar{T}\exp[-i\int_0^t H(t')dt']$ where "$T$ with the arrow on top" is the "Dyson time-ordering operator".

In practice, this is just fancy notation for the idea of dividing $t$ into many short time periods, during which $H(t)$ is nearly constant, and representing $U(t)$ by

$$U(t) \approx e^{-iH_M \delta t} e^{-iH_{M-1} \delta t} e^{-iH_{M-2} \delta t} ... e^{-iH_2 \delta t} e^{-iH_1 \delta t} e^{-iH_0 \delta t}$$
How do we calculate NMR signals?

In quantum mechanical terms, signals are "observables", and observable quantities are represented by Hermitian operators. The "expectation value" of an observable \( O \) in a pure state \( |\psi(t)\rangle \) at time \( t \) is \( o(t) = \langle \psi(t) | O | \psi(t) \rangle \).

If \( |\psi(t)\rangle \) happens to be an eigenstate of \( O \) with eigenvalue \( x \), then \( o(t) = \langle \psi(t) | O | \psi(t) \rangle = x \langle \psi(t) | \psi(t) \rangle = x \).

If \( |\psi(t)\rangle \) is a linear combination of eigenstates \( |n\rangle \) with eigenvalues \( x_n \), such as
\[
|\psi(t)\rangle = \sum_{n=1}^{N} a_n(t) |n\rangle,
\]
then
\[
o(t) = \sum_{n,n'=1}^{N} a_n(t)^* a_n(t) \langle n'| O | n \rangle = \sum_{n,n'=1}^{N} a_n(t)^* a_n(t) x_n \langle n'| n \rangle = \sum_{n=1}^{N} |a_n(t)|^2 x_n
\]
So \( o(t) \) is a weighted average of the eigenvalues of \( O \), weighted by the relative populations of the eigenstates.

For a mixed state, the expectation value becomes \( o(t) = \langle \psi(t) | O | \psi(t) \rangle \), where the bar over the top again means an average over "many copies". Using the fact that \( \sum_{n=1}^{N} |n\rangle \langle n| = 1 \) for any orthonormal basis \( \{ |n\rangle \} \), we can express \( o(t) \) as:
\[
o(t) = \sum_{n=1}^{N} \langle \psi(t) | n \rangle \langle n | O | \psi(t) \rangle = \sum_{n=1}^{N} \langle n | O | \psi(t) \rangle \langle \psi(t) | n \rangle = \sum_{n=1}^{N} \langle n | O | \psi(t) \rangle \langle \psi(t) | n \rangle
\]
\[
= \sum_{n=1}^{N} \langle n | O \rho(t) | n \rangle \equiv \text{Tr}\{ O \rho(t) \}
\]
where \( \text{Tr}\{A\} \) is the "trace" of \( A \), equal to the sum of the diagonal elements of \( A \) (in any basis).
How do we calculate NMR signals?

In NMR, signals arise from oscillating magnetic flux in the rf coil (antenna) of our NMR probe, due to precessing nuclear spin magnetization. Magnetization is proportional to spin angular momentum (through the gyromagnetic ratio). The NMR signals $F_{lab}(t)$ (in the laboratory frame) are then proportional to one of the transverse angular momentum components, $S_x$.

Therefore, $F_{lab}(t) \propto \text{Tr}\{S_x \rho(t)\} = \text{Tr}\{S_x U(t)\rho(0)U(t)^{-1}\} \propto \text{Tr}\{S_x U(t)S_z U(t)^{-1}\}$

As you may know, NMR signals are apparently detected in the rotating frame, and we measure both $x$ and $y$ components of the spin magnetization, or "real" and "imaginary" components. Where does this come from?

The transformation into a rotating frame in NMR is a special case of a more general transformation of reference system, which is described in quantum mechanics by some unitary operator $A(t)$. If states in the original reference system are $|\psi(t)\rangle$, then states in the new reference system are $|\psi'(t)\rangle = A(t)|\psi(t)\rangle$. Similarly, $\rho'(t) = A(t)\rho(t)A(t)^{-1}$.

What are the Hamiltonian and the evolution operator in the new reference system?

$$i \frac{d}{dt} |\psi'(t)\rangle = i \frac{d}{dt} [A(t)|\psi(t)\rangle] = i \frac{dA(t)}{dt} |\psi(t)\rangle + A(t)[i \frac{d}{dt} |\psi(t)\rangle]$$

$$= i \frac{dA(t)}{dt} |\psi(t)\rangle + A(t)H(t)|\psi(t)\rangle$$

$$= \left( i \frac{dA(t)}{dt} A(t)^{-1} + A(t)H(t)A(t)^{-1} \right) |\psi'(t)\rangle \equiv H'(t)|\psi'(t)\rangle$$

$H'(t)$ is the transformed Hamiltonian. Note that it includes an extra term, sometimes called a fictitious field (or a gauge field). $U'(t)$ is the evolution operator generated by $H'(t)$. 
How do we calculate NMR signals?

The rotating frame in NMR is the transformation brought about $A(t) = \exp(iS_z \omega_{rf}t)$, in other words by a rotation of spin angular momenta about $z$ at the rf carrier frequency (opposite to the direction of precession).

If $H(t) = H_Z + H_{rf}(t) + H_{int}(t)$ in the laboratory frame, with $H_Z = \omega_0 S_z$ and $H_{rf}(t) = 2\omega_1 \cos(\omega_{rf}t-\phi)S_x$, then

$$H'(t) = i\frac{d(e^{iS_z \omega_{rf}t})}{dt} e^{-iS_z \omega_{rf}t} + e^{iS_z \omega_{rf}t}(\omega_0 S_z) e^{-iS_z \omega_{rf}t} + e^{iS_z \omega_{rf}t}[2\omega_1 \cos(\omega_{rf}t-\phi)S_x] e^{-iS_z \omega_{rf}t} + e^{iS_z \omega_{rf}t}H_{int}(t)e^{-iS_z \omega_{rf}t}$$

$$=-\omega_{rf}S_z + \omega_0 S_z + 2\omega_1 \cos(\omega_{rf}t-\phi)(S_x \cos \omega_{rf}t - S_y \sin \omega_{rf}t) + \tilde{H}_{int}(t)$$

$$=(\omega_0 - \omega_{rf})S_z + 2\omega_1 (\cos \omega_{rf}t \cos \phi + \sin \omega_{rf}t \sin \phi)(S_x \cos \omega_{rf}t - S_y \sin \omega_{rf}t) + \tilde{H}_{int}(t)$$

$$\approx \Delta \omega S_z + \omega_1 (S_x \cos \phi + S_y \sin \phi) + \tilde{H}_{int}(t)$$

The last line follows by taking the time averages of terms like $\cos \omega_{rf}t \cos \omega_{rf}t$ and $\cos \omega_{rf}t \sin \omega_{rf}t$, which are $1/2$ and zero, respectively. This is the "rotating frame approximation" or the "rotating wave approximation".

$\Delta \omega$ is the resonance offset. The rf term now looks the way we expect. More will be said about $H_{int}(t)$ later.
How do we calculate NMR signals?

The evolution operator in the rotating frame is $U'(t)$, generated by $H'(t)$. But the evolution operator in the laboratory frame can now be written as $U(t)=A(t)^{-1}U'(t)=\exp(-iS_z\omega_{rf}t)U'(t)$.

Returning to the expression for the NMR signals:

$$F_{\text{lab}}(t) \propto \text{Tr}\{S_x U(t)S_z U(t)^{-1}\} = \text{Tr}\{S_x R_z(\omega_{rf}t)U'(t)S_z U'(t)^{-1}R_z(-\omega_{rf}t)\}$$

$$= \text{Tr}\{R_z(-\omega_{rf}t)S_x R_z(\omega_{rf}t)U'(t)S_z U'(t)^{-1}\}$$

$$= \text{Tr}\{(S_x \cos\omega_{rf}t - S_y \sin\omega_{rf}t)U'(t)S_z U'(t)^{-1}\}$$

$$= \text{Tr}\{S_x U'(t)S_z U'(t)^{-1}\} \cos\omega_{rf}t - \text{Tr}\{S_y U'(t)S_z U'(t)^{-1}\} \sin\omega_{rf}t$$

$$= F_{\text{real}}(t) \cos\omega_{rf}t + F_{\text{imag}}(t) \sin\omega_{rf}t$$

NMR spectrometers are constructed to measure separately the $\cos\omega_{rf}t$ and $\sin\omega_{rf}t$ terms, so in the end we get the expected real and imaginary signals in the rotating frame, where precession around $z$ occurs at frequency $\Delta \omega$, where rf pulses look like rotations around $x$ or $y$ for $\phi = 0$ or $\phi = \pi/2$, and where the internal spin interactions are changed to $\tilde{H}_{\text{int}}(t)$.
Nuclear spin interactions that affect solid state NMR

$H_{\text{int}}(t)$ contains magnetic dipole-dipole interactions ($H_D$), anisotropic chemical shifts ($H_{\text{CSA}}$), scalar couplings ($H_J$), and electric quadrupole couplings ($H_Q$). Other interactions are important in solid state physics, but are not relevant to biomolecular solid state NMR of non-paramagnetic samples. For now, we will focus on $H_D$ and $H_{\text{CSA}}$.

Dipole-dipole interaction between two magnetic moments $\mu_1$ and $\mu_2$, with $\mu = \gamma S$:

$$H_D = -\left[\frac{3(\mu_1 \cdot r)(\mu_2 \cdot r)}{r^5} - \frac{\mu_1 \cdot \mu_2}{r^3}\right] = -\gamma_1 \gamma_2 \left[\frac{3(S_1 \cdot r)(S_2 \cdot r)}{r^2} - S_1 \cdot S_2\right]$$

$$= \frac{3\gamma_1 \gamma_2}{r^3} \sum_{m=-2}^{2} (-1)^m Y_{2m}(\theta, \phi) T_{2-m}$$

Angles $\theta$ and $\phi$ specify the direction of the internuclear vector in the current axis system. The internuclear distance is $r$.

**spherical harmonic functions**

$$Y_{20} = \frac{1}{\sqrt{6}} (3 \cos^2 \theta - 1)$$

$$Y_{2\pm 1} = \mp \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_{2\pm 2} = \frac{1}{2} \sin^2 \theta e^{\pm 2i\phi}$$

**irreducible tensor operators**

$$T_{20} = \frac{1}{\sqrt{6}} (3S_{z1}S_{z2} - S_1 \cdot S_2)$$

$$= \frac{1}{\sqrt{6}} [2S_{z1}S_{z2} - \frac{1}{2} (S_{+1}S_{-2} + S_{-1}S_{+2})]$$

$$T_{2\pm 1} = \mp \frac{1}{2} (S_{z1}S_{\pm 2} + S_{z2}S_{\pm 1})$$

$$T_{2\pm 2} = \frac{1}{2} S_{\pm 1}S_{\pm 2}$$
Irreducible tensor operators (and spherical harmonics) transform among themselves under rotations, which makes them useful for understanding how rotations affect the spin interactions.

In particular, if a new axis system $x'y'z'$ is related to an original axis system $xyz$ by Euler angles $\alpha, \beta, \gamma$, then $T_{2m}$ in the original axis system turns into $\tilde{R}(\alpha \beta \gamma)T_{2m}$ in the new axis system, with:

$$\tilde{R}(\alpha \beta \gamma)T_{2m} = \sum_{m'=-2}^{2} D^{(2)}_{m'm} (-\gamma, -\beta, -\alpha) T_{2m'}$$

where $D^{(2)}_{m'm}$ is a "Wigner rotation matrix element", defined by

$$D^{(s)}_{m'm}(\alpha, \beta, \gamma) = \langle sm' | e^{-iS_z \alpha} e^{-iS_y \beta} e^{-iS_z \gamma} | sm \rangle \quad \text{for a spin-$s$ particle.}$$

Also, $D^{(s)}_{m'm}(\alpha, \beta, \gamma) = e^{-im'\alpha} d^{(s)}_{m'm}(\beta) e^{-im\gamma}$, where $d^{(2)}_{m'm}$ is a "reduced Wigner rotation matrix element".

Irreducible tensors have the important property that $e^{iS_z \theta} T_{2m} e^{-iS_z \theta} = e^{im\theta} T_{2m}$

(Note: I use $\tilde{R}$ above to represent a "passive" rotation, meaning that we change the orientation of the axis system and then ask "What does $T_{2m}$ look like in the new axis system?" This is the opposite of keeping the axis system fixed, rotating $T_{2m}$, and then asking "What has $T_{2m}$ turned into?", which would be an "active" rotation.)
In a non-spinning sample (and without molecular motions), $H_D$ is constant. If there are no other interactions except $H_z$, the full rotating-frame Hamiltonian is

$$H = \Delta \omega S_z + \tilde{H}_{\text{int}}(t)$$

$$= \Delta \omega S_z + e^{iS_z\omega_{rf}t}H_D e^{-iS_z\omega_{rf}t}$$

$$= \Delta \omega S_z + \frac{3\gamma_1\gamma_2}{r^3} \sum_{m=-2}^{2} (-1)^m Y_{2m}(\theta, \phi)e^{iS_z\omega_{rf}t}T_{2-m} e^{-iS_z\omega_{rf}t}$$

$$= \Delta \omega S_z + \frac{3\gamma_1\gamma_2}{r^3} \sum_{m=-2}^{2} (-1)^m Y_{2m}(\theta, \phi)e^{-im\omega_{rf}t}T_{2-m}$$

$$\approx \Delta \omega S_z + \frac{3\gamma_1\gamma_2}{r^3} Y_{20}(\theta, \phi)T_{20} = \Delta \omega S_z + \frac{\gamma_1\gamma_2}{r^3} \frac{(3\cos^2\theta - 1)}{2} (3S_z S_{z2} - S_1 \cdot S_2)$$

This is the familiar homonuclear dipole-dipole coupling.

The dipole-dipole coupling Hamiltonian is "truncated" by the large external field along $z$, so that only the part of $H_D$ that commutes with $S_z$ affects NMR signals. In this treatment, truncation occurs because $\exp(-im\omega_{rf}t)$ averages to zero in the rotating frame unless $m = 0$. So only the $T_{20}$ term survives.
In the heteronuclear case, spins 1 and 2 have very different values of $\Delta \omega$, so

$$H = \Delta \omega_1 S_{z1} + \Delta \omega_2 S_{z2} + \frac{\gamma_1 \gamma_2}{r^3} \frac{(3 \cos^2 \theta - 1)}{2} (3S_{z1}S_{z2} - S_1 \cdot S_2)$$

$$= \frac{\Delta \omega_1 + \Delta \omega_2}{2} (S_{z1} + S_{z2}) + \frac{\Delta \omega_1 - \Delta \omega_2}{2} (S_{z1} - S_{z2}) + \frac{\gamma_1 \gamma_2}{r^3} \frac{(3 \cos^2 \theta - 1)}{2} (3S_{z1}S_{z2} - S_1 \cdot S_2)$$

$$= \frac{(\Delta \omega_1 + \Delta \omega_2)}{2} (S_{z1} + S_{z2}) + \frac{(\Delta \omega_1 - \Delta \omega_2)}{2} (S_{z1} - S_{z2})$$

$$+ \frac{\gamma_1 \gamma_2}{r^3} \frac{(3 \cos^2 \theta - 1)}{2} [2S_{z1}S_{z2} - \frac{1}{2} (S_{+1}S_{-2} + S_{-1}S_{+2})]$$

If we transform to a frame of reference defined by $A(t) = \exp(iH_{\text{diff}} t)$, where $H_{\text{diff}}$ is the term proportional to $S_{z1}-S_{z2}$, we find that the "flip-flop" term in the dipole-dipole coupling (i.e., the term involving $S_{+1}S_{-2} + S_{-1}S_{+2}$) looks rapidly oscillatory. This term then averages out. Transforming back, we get

$$H \approx \Delta \omega_1 S_{z1} + \Delta \omega_2 S_{z2} + \frac{\gamma_1 \gamma_2}{r^3} (3 \cos^2 \theta - 1) S_{z1}S_{z2}$$

This is the familiar heteronuclear dipole-dipole coupling. It is appropriate whenever the difference between NMR frequencies of spins 1 and 2 greatly exceeds the strength of the dipole-dipole coupling.
Nuclear spin interactions that affect solid state NMR

That was for a non-spinning sample.

We saw that a large external field along z truncates the dipole-dipole coupling. But for a spinning sample, the direction of the external field relative to the sample is changing with time, so we cannot truncate $H_D$ right away.

For magic-angle spinning (MAS) experiments, we must first determine how $H_D$ is affected by spinning, before truncating it.

To do this, we transform from a "molecule-fixed" axis system, to a "rotor-fixed" axis system, and then to the laboratory axis system (where the external field is along z). Then we can truncate the coupling.
Nuclear spin interactions that affect solid state NMR

\[ H_D = \frac{3\gamma_1\gamma_2}{r^3} \sum_{m=-2}^{2} (-1)^m Y_{2m}(\theta, \phi) T_{2-m} \]

\[ \downarrow \tilde{R}(\alpha, \beta, \gamma = \text{arbitrary}) \downarrow \]

\[ \frac{3\gamma_1\gamma_2}{r^3} \sum_{m',m=-2}^{2} (-1)^m Y_{2m}(\theta, \phi)e^{-im\alpha}e^{im'\gamma}d^{(2)}_{m',-m}(-\beta)T_{2m'} \]

\[ \downarrow \tilde{R}(\alpha = \omega_R t, \beta = \theta_m, \gamma = 0) \downarrow \]

\[ \frac{3\gamma_1\gamma_2}{r^3} \sum_{m'',m',m=-2}^{2} (-1)^m Y_{2m}(\theta, \phi)e^{-im\alpha}e^{im'\gamma}d^{(2)}_{m',-m}(-\beta)e^{im'\omega_R t}d^{(2)}_{m'',m'}(-\theta_m)T_{2m''} \]

\[ \downarrow \text{truncate} \downarrow \]

\[ \frac{3\gamma_1\gamma_2}{r^3} \sum_{m',m=-2}^{2} (-1)^m Y_{2m}(\theta, \phi)e^{-im\alpha}e^{im'(\omega_R t + \gamma)}d_{m',-m}(-\beta)d_{0,m'}(-\theta_m)T_{20} \]

Note that \( d^{(2)}_{0,0}(\pm \theta_m) = 0 \). So \( H_D \) contains only terms that oscillate at \( \omega_R \) and \( 2\omega_R \), and therefore averages to zero at the magic angle.

(Unless we also apply rf pulse sequences)
Anisotropic chemical shifts have the form $H_{CSA} = \omega_0 \mathbf{B} \cdot \mathbf{\tilde{\sigma}} \cdot \mathbf{S}$, where $\mathbf{\tilde{\sigma}}$ is a $3 \times 3$ CSA matrix.

This means that any component of the magnetic field $\mathbf{B}$ couples to any component of the spin angular momentum $\mathbf{S}$.

But in the principal axis system of the CSA matrix, where this matrix is purely diagonal:

$$H_{CSA} = \omega_0 (\sigma_x B_x S_x + \sigma_y B_y S_y + \sigma_z B_z S_z)$$

$$= \omega_0 (\sigma_1 B_x S_x + \sigma_2 B_y S_y + \sigma_3 B_z S_z) + \omega_0 \sigma_{iso} \mathbf{B} \cdot \mathbf{S}$$

$$\sigma_{iso} = (\sigma_x + \sigma_y + \sigma_z)/3$$ is the isotropic shift (or shielding), and $\sigma_1 + \sigma_2 + \sigma_3 = 0$

$H_{CSA}$ in its principal axis system can then be rewritten as:

$$H_{CSA} = \omega_0 \sigma_3 \left[ (B_z S_z - \frac{1}{2} B_x S_x - \frac{1}{2} B_y S_y) + \frac{1}{2} \frac{\sigma_1 - \sigma_2}{\sigma_3} (B_x S_x - B_y S_y) \right] + \omega_0 \sigma_{iso} \mathbf{B} \cdot \mathbf{S}$$

$$= \omega_0 \sqrt{6} \sigma_3 T_{20} + \omega_0 \eta \sigma_{33} (T_{22} + T_{2-2}) + \omega_0 \sigma_{iso} \mathbf{B} \cdot \mathbf{S}$$

Then MAS can be analyzed in the same way as for dipole-dipole couplings to get $H_{CSA}$ in the laboratory frame. Again, the anisotropic part oscillates at $\omega_R$ and $2\omega_R$, but with an extra term due to the asymmetry parameter $\eta = (\sigma_1 - \sigma_2)/\sigma_3$. The isotropic part becomes $\omega_0 \sigma_{iso} B_z S_z$. 
Manipulation of spin interactions by rf pulses and sample spinning

Pulse sequences, together with sample rotation, can be used to change the form of spin interactions and to turn various interactions on and off.

As a simple example, consider a homonuclear two-spin system with a dipole-dipole coupling and with chemical shifts, subjected to the following pulse sequence:

\[
\tau/2 \quad 180_X \quad \tau/2 \quad 180_X
\]

The evolution operator for this sequence is

\[
U(\tau) = R_x(-\pi)e^{-i(H_D + H_{CSA})\tau/2}R_x(\pi)e^{-i(H_D + H_{CSA})\tau/2}
\]

where \(H_D\) and \(H_{CSA}\) are now taken to be in their high-field, truncated forms.

This can be rewritten as

\[
U(\tau) = e^{-i[R_x(-\pi)(H_D + H_{CSA})R_x(\pi)]\tau/2}e^{-i(H_D + H_{CSA})\tau/2}
\]

\[
= e^{-i(\tilde{H}_D + \tilde{H}_{CSA})\tau/2}e^{-i(H_D + H_{CSA})\tau/2}
\]

which looks like the evolution operator for:

\[
\tilde{H}_D + \tilde{H}_{CSA} \quad H_D + H_{CSA}
\]
Manipulation of spin interactions by rf pulses and sample spinning

Since $H_D$ is proportional to $(3S_{z1}S_{z2} - S_1 \cdot S_2)$ and $H_Z$ is proportional to $\delta_1 S_{z1} + \delta_2 S_{z2}$:

$$\tilde{H}_D = H_D \quad \text{and} \quad \tilde{H}_Z = -H_Z$$

Strictly speaking, $[H_D + H_Z, H_D - H_Z] \neq 0$, so it is not precisely true that

$$e^{-i(\tilde{H}_D + \tilde{H}_{CSA})\tau/2} e^{-i(H_D + H_{CSA})\tau/2} \approx e^{-i(\tilde{H}_D + \tilde{H}_{CSA} + H_D + H_{CSA})\tau/2}$$

$$= e^{-iH_D\tau} = U(\tau)$$

However, this is a good approximation as long as $\tau$ is small (compared with the inverse of the dipole-dipole coupling strength and the chemical shift difference).

So the net effect of this simple pulse sequence is to make the Hamiltonian in the second $\tau/2$ period different from the Hamiltonian in the first $\tau/2$ period. And the pulses themselves vanish. If $\tau$ is sufficiently small, the overall evolution operator is determined by an "effective" Hamiltonian, given (to a lowest-order approximation) by the time-average of the Hamiltonian.

This is essentially how average Hamiltonian theory (AHT) works. In this simple example, the effective Hamiltonian is just $H_D$. $H_Z$ is averaged out by the pulses.
The more abstract description of AHT is as follows:

Consider a rotating frame Hamiltonian of the form $H(t) = H_{\text{int}}(t) + H_{\text{RF}}(t)$. $H(t)$ generates the evolution operator $U(t)$. $H_{\text{RF}}(t)$ by itself generates the evolution operator $U_{\text{RF}}(t)$, which is a rotation operator, since rf pulses produce rotations.

Imagine that the rf pulse sequence consists of a block of pulses, with length $\tau_c$ called the "cycle time", that is repeated many times. We are interested in the evolution operator for one complete cycle $U(\tau_c)$.

We are also interested in pulse sequences where the net rotation over one block is zero (or a multiple of $2\pi$), so that the pulses alone would have no net effect at multiples of $\tau_c$.

Thus, $U_{\text{RF}}(\tau_c) = 1$.

We transform to a frame of reference defined by $A(t) = U_{\text{RF}}(t)^{-1}$ and recall the following result for the Hamiltonian in the transformed frame:

$$H'(t) = i \frac{d}{dt} U_{\text{RF}}(t)^{-1} U_{\text{RF}}(t) + U_{\text{RF}}(t)^{-1} H(t) U_{\text{RF}}(t)$$
Manipulation of spin interactions by rf pulses and sample spinning

It can be shown that
\[ i \frac{dU_{RF}(t)^{-1}}{dt} U_{RF}(t) = -H_{RF}(t) \]

Therefore,
\[ H'(t) = U_{RF}(t)^{-1} H_{int}(t) U_{RF}(t) = H_{int}'(t) \]

The overall evolution operator becomes \( U(t) = U_{RF}(t)U'_{int}(t) \), so that \( U(\tau_c) = U'_{int}(\tau_c) \).

Therefore,
\[ U(\tau_c) = \hat{T} \exp[-i\int_0^{\tau_c} H_{int}'(t')dt'] \]

If \( H_{int}'(t) \) commutes with itself at all times, then
\[ U(\tau_c) = \exp[-i\int_0^{\tau_c} H_{int}'(t')dt'] = \exp(-iH_{ave}' \tau_c) \]

\[ H_{ave}' = \frac{1}{\tau_c} \int_0^{\tau_c} H_{int}'(t')dt' \]

More generally, \( U(\tau_c) \) can be expressed as \( \exp(-iH_{eff}\tau_c) \), with the effective Hamiltonian represented by a "Magnus expansion":

\[ H_{eff} = H^{(0)} + H^{(1)} + H^{(2)} + ... \]

\[ H^{(0)} = H_{ave}' \]

\[ H^{(1)} = -\frac{1}{2\tau_c} \int_0^{\tau_c} dt' \int_0^{t'} [H'_{int}(t'), H'_{int}(t'')] \]
Manipulation of spin interactions by rf pulses and sample spinning

Things to remember:

AHT applies only to pulse sequences that are "periodic and cyclic", in other words repetitive and with $U(\tau_c) = 1$. So, for example, it is not used much in solution NMR, where such pulse sequences are rare.

AHT only provides information about the effective Hamiltonian, and hence the NMR signals, at multiples of the cycle time $\tau_c$. So, for example, it does not provide information about spinning sidebands, or other effects due to variations within the cycle time.

AHT works well only when $1/\tau_c$ is large compared to the size of $H_{\text{int}}$ (or when $H_{\text{int}}'(t)$ commutes with itself at all times).

AHT has been very important in the development of modern solid state NMR.
Homonuclear Dipolar Recoupling in Solid State NMR: Analysis with Average Hamiltonian Theory


Robert Tycko
Building 5, Room 112
National Institutes of Health
Bethesda, MD  20892-0520
phone: 301-402-8272; e-mail: robertty@mail.nih.gov

Definition of homonuclear recoupling
Pulse sequences that create non-zero effective (i.e., average) dipole-dipole couplings among like spins (e.g., $^{13}$C-$^{13}$C couplings) during magic-angle spinning (MAS).

Motivations for homonuclear recoupling (partial list)
(1) to measure distances between like nuclei
(2) to produce crosspeaks between like nuclei in 2D or 3D MAS NMR spectra
(3) to permit double-quantum filtering, for selective observation of NMR signals arising from pairs or groups of dipole-coupled nuclei
(4) to permit spin polarization transfers, as required for various other structural techniques (e.g., "tensor correlation" techniques)

Why are pulse sequences necessary?
MAS is usually required for sufficient resolution and sensitivity in solid state NMR of unoriented systems. MAS produces narrow lines by averaging out anisotropy of chemical shifts and magnetic dipole-dipole couplings. Recoupling sequences are needed to restore these interactions.
Outline

I. Relevant quantum mechanical principles

II. Useful mathematical identities and tricks

III. Nuclear spin interactions under MAS

IV. Average Hamiltonian Theory in simple terms

V. Homonuclear dipolar recoupling mechanisms
   A. Delta-function pulse sequences
   B. Continuous rf irradiation
   C. Finite-pulse recoupling sequences
   D. Chemical-shift-driven recoupling

VI. Symmetry principles for recoupling sequences

Appendix: Derivation of time-dependent dipole-dipole coupling under MAS

13C NMR spectra of uniformly 15N, 13C-labeled L-valine powder, obtained in a 14.1 T magnetic field at the indicated MAS frequencies.
DISCLAIMERS:

1. THE PRESENTATION OF DIPOLAR RECOUPLING TECHNIQUES AND OTHER TOPICS IN THESE NOTES IS MOTIVATED SOLELY BY PEDAGOGICAL CONSIDERATIONS. MANY USEFUL TECHNIQUES AND BRILLIANT IDEAS ARE OMITTED, AND MANY IMPORTANT PAPERS ARE NOT CITED. THE GOAL OF THESE NOTES IS SOLELY TO SUMMARIZE THE THEORETICAL/MATHEMATICAL BACKGROUND REQUIRED FOR AN UNDERSTANDING OF DIPOLAR RECOUPLING AND RELATED TECHNIQUES IN SOLID STATE NMR.

2. THESE NOTES MAY CONTAIN MISTAKES. PLEASE LET ME KNOW IF YOU NOTICE ANYTHING THAT SEEMS TO BE INCORRECT.
I. Relevant quantum mechanical principles

If a spin system is in a single, well-defined state, that state is represented by a state vector $|\psi(t)\rangle$. For example, a system of three spin-1/2 nuclei could be in the state $|\psi(0)\rangle = |++-\rangle$ at time $t = 0$.

The evolution of $|\psi(t)\rangle$ with time is determined by the Schrödinger equation:

$$i \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle \quad (I.1)$$

where $H(t)$ is the Hamiltonian operator (in angular frequency units), which contains terms that represent each of the nuclear spin interactions. If $H(t)$ is constant (i.e., $H(t) = H$), then Eq. (I.1) has the solution

$$|\psi(t)\rangle = e^{-iHt} |\psi(0)\rangle \quad (I.2)$$

If $H(t)$ is not constant, the solution to Eq. (I.1) is

$$|\psi(t)\rangle = U(t) |\psi(0)\rangle \quad (I.3a)$$

$$U(t) = T \exp \left\{ -i \int_0^t dt' H(t') \right\} \quad (I.3b)$$

where $T$ is the Dyson time-ordering operator. $U(t)$ is the evolution operator. If the time interval from 0 to $t$ is divided into $N$ intervals with lengths $\tau_j$ during which the Hamiltonian is $H_j$, Eq. (I.3b) is short-hand for

$$U(t) = e^{-iH_N \tau_N} e^{-iH_{N-1} \tau_{N-1}} \ldots e^{-iH_2 \tau_2} e^{-iH_1 \tau_1} \quad (I.3c)$$

which is simply an extension of Eq. (I.2). Also, Eqs. (I.1) and (I.3a) imply

$$i \frac{d}{dt} U(t) = H(t) U(t) \quad (I.4)$$

Signals in quantum mechanics are "expectation values" of Hermitian operators, evaluated according to

$$S_A(t) = \langle \psi(t) | A | \psi(t) \rangle \quad (I.5)$$

$|\psi(t)\rangle$ and $<\psi(t)|$ are called "ket" and "bra" vectors.
In actual calculations, Eq. (I.5) would be evaluated by choosing a complete basis of states for the system, \{|n\rangle\}, that satisfies \( <n|n'\rangle = \delta_{n,n'} \). \(|\psi(t)\rangle\) would be represented as a column vector with elements \( <n|\psi(t)\rangle \). \(<\psi(t)|\) would be represented by a row vector with elements \( <n|\psi(t)\rangle \). \(|A\rangle\) would be a matrix with elements \( <n|A|m\rangle \) in the \( n^{th} \) row and \( m^{th} \) column.

In NMR, we don't usually have spin systems in single, well-defined states. Therefore, we use density operators instead of state vectors. The density operator is defined as

\[
\rho(t) = |\psi(t)\rangle\langle\psi(t)|
\]  

(I.6)

where the bar represents a weighted average over the spin states that are present in the sample. It can be shown that Eq. (I.1) implies that \(\rho(t)\) satisfies the equation

\[
i\frac{d}{dt}\rho(t) = [H(t),\rho(t)]
\]  

(I.7)

where \([A,B] \equiv AB - BA\) means the commutator of operator \(A\) and operator \(B\). Eq. (I.7) implies

\[
\rho(t) = U(t)\rho(0)U(t)^{-1}
\]  

(I.8)

We usually assume that the initial condition \(\rho(0)\) before applying our pulse sequence is proportional to the sum of the \(z\) components of spin angular momentum for the relevant nuclei, i.e., \(\rho(0) \propto I_z = \sum_k I_{zk} \). This is appropriate at normal temperatures when the spins are at thermal equilibrium in a strong magnetic field along \(z\).

Signals are

\[
S_A(t) = \text{Tr}\{A\rho(t)\}
\]  

(I.9)

where \(\text{Tr}\{B\}\) is the trace of operator \(B\), defined as \(\text{Tr}\{B\} = \sum_n <n|B|n\rangle\) if \{|n\rangle\} is a basis of states as discussed above. Conventional NMR signals are proportional to the transverse components of spin angular momentum. In the rotating frame, the NMR signals have real and imaginary parts, proportional to \(I_x = \sum_k I_{xk}\) and \(I_y = \sum_k I_{yk}\). These are usually combined into one complex signal \(S(t)\), which is then

\[
S(t) = S_{\text{real}}(t) + iS_{\text{imag}}(t)
\]

\[
\propto \text{Tr}\{I_x\rho(t)\} + i\text{Tr}\{I_y\rho(t)\}
\]

\[
= \text{Tr}\{I_+\rho(t)\}
\]

\[
= \text{Tr}\{I_+U(t)I_zU(t)^{-1}\}
\]  

(I.10)
where $I_z = I_x \pm iI_y$ and $U(t)$ is the evolution operator for the nuclear spin system, resulting from a combination of interactions with rf pulses and internal spin interactions.

II. Useful mathematical identities and tricks

If $A$, $B$, and $C$ are normal quantum mechanical operators, then

$$\text{Tr}\{ABC\} = \text{Tr}\{CAB\}$$

(II.1)

If the operator $A$ has an inverse $A^{-1}$, such that $AA^{-1} = 1$, then

$$\text{Tr}\{B\} = \text{Tr}\{ABA^{-1}\}$$

(II.2)

$$A e^{B A^{-1}} = e^{ABA^{-1}}$$

(II.3)

If $I_x$, $I_y$, and $I_z$ are the operators for the x, y, and z components of spin angular momentum, then rotations of spin angular momentum (for example, by rf pulses) are expressed mathematically by equations such as

$$e^{-iI_x \theta} I_y e^{iI_x \theta} = I_y \cos \theta + I_z \sin \theta$$

(II.4a)

$$e^{-iI_x \theta} I_z e^{iI_x \theta} = I_z \cos \theta - I_y \sin \theta$$

(II.4b)

The same equations hold if the following substitutions are made: $\{I_x \rightarrow I_y, I_y \rightarrow I_z, \text{and} I_z \rightarrow I_x\}$ or $\{I_x \rightarrow I_z, I_y \rightarrow I_x, \text{and} I_z \rightarrow I_y\}$. These are cyclic permutations of x, y, and z.

It is often useful to represent spin angular momenta by raising and lowering operators, which have the properties

$$I_\pm \equiv I_x \pm iI_y$$

(II.5a)

$$e^{-iI_z \theta} I_\pm e^{iI_z \theta} = e^{\mp i\theta} I_\pm$$

(II.5b)

When two operators $A$ and $B$ satisfy $AB = BA$, these operators are said to commute with one another. In general, quantum mechanical operators do not commute with one another. In other words, $[A, B] \equiv AB - BA \neq 0$. This means they can not be permuted without changing the result. However, if $B$ has an inverse $B^{-1}$, then permutations can be accomplished (i.e., the order or grouping of $A$ and $B$ can be rearranged) by using the following trick:

$$AB = BA'$$

(II.6a)

$$A' = B^{-1} AB$$

(II.6b)
Therefore, if you have a set of \( N \) operators \( \{ A_j \} \) and a set of \( N \) invertible operators \( \{ B_j \} \), by applying Eqs. (II.6a,b) repeatedly, you can show that

\[
A_N B_N A_{N-1} B_{N-1} A_{N-2} B_{N-2} \ldots A_2 B_2 A_1 = B_N B_{N-1} B_{N-2} \ldots B_2 B_1 A_N ' A_{N-1} ' A_{N-2} ' \ldots A_2 ' A_1 ' \\
(II.7a)
\]

\[
A_k ' = B_1 ^{-1} B_2 ^{-1} \ldots B_{k-2} ^{-1} B_{k-1} ^{-1} B_k ^{-1} A_k B_k B_{k-1} B_{k-2} \ldots B_2 B_1 \\
(II.7b)
\]

Eqs. (II.7a,b) are one of the keys to understanding Average Hamiltonian Theory and recoupling sequences, as shown below. These equations show that all of the operators \( \{ B_j \} \) can be pulled to one side, leaving the operators \( \{ A_j \} \) on the other side, but in the altered form \( \{ A_j ' \} \).

As mentioned above, actual calculations or numerical simulations are usually performed by choosing a complete basis of states for the system, \( \{ |n> \} \), that satisfies \( < n | n' > = \delta_{n,n} \) and representing the density operator, Hamiltonian, and other operators as \( N \times N \) matrices (where \( N \) is now the number of states in the basis set). For an operator \( A \), the number in the \( n \)th row and \( m \)th column would be \( < n | A | m > \). In general, \( < n | A | m > \) is a complex number. The adjoint of \( A \) is another operator \( A^\dagger \) with matrix elements \( < n | A^\dagger | m > = < m | A | n >^* \).

A Hermitian operator is one for which \( A = A^\dagger \), or \( < n | A | m > = < m | A | n >^* \). In quantum mechanics, \( H \), \( \rho \), and all operators that represent observable quantities are Hermitian.

A unitary operator is one for which \( A^{-1} = A^\dagger \), which implies that

\[
\sum_{m=1}^{N} < n | A | m > < m | A | n'^* = \delta_{n,n'} . \quad \text{Quantum mechanical evolution operators } U(t) \text{ are unitary.}
\]

In general, if \( A \) is Hermitian, then \( e^{iA} \) and \( e^{-iA} \) are unitary. Angular momentum operators \( I_x \), \( I_y \), and \( I_z \) (but not \( I_+ \) and \( I_- \)) are Hermitian, so rotation operators (e.g., \( e^{-iI_x \theta} \)) are unitary.

For non-commuting operators,

\[
(ABC)^\dagger = C^\dagger B^\dagger A^\dagger \quad \text{(II.8a)}
\]

\[
(ABC)^{-1} = C^{-1} B^{-1} A^{-1} \quad \text{(II.8b)}
\]

According to Eqs. (II.8), we must reverse the order of noncommuting operators when we take the adjoint or inverse of a product of these operators.

In general, if \( [A,B] \neq 0 \), then \( e^{A} e^{B} \neq e^{A+B} \neq e^{B} e^{A} \) (or \( e^{iA} e^{iB} \neq e^{i(A+B)} \neq e^{iB} e^{iA} \) if we are concerned with making unitary operators from Hermitian operators \( A \) and \( B \)). However, if both \( A \) and \( B \) are very small, then the following approximations can be made:

\[
e^{A} e^{B} \approx e^{A+B} \approx e^{B} e^{-A} \quad \text{(II.9)}
\]
On the other hand, if \([A,B] = 0\), Eqs. (II.9) are exactly true even if \(A\) and/or \(B\) are not small.

### III. Nuclear spin interactions under MAS

NMR experiments are performed in the rotating frame. For present purposes, we assume that the nuclear spin Hamiltonian in the rotating frame contains only four terms, representing homonuclear dipole-dipole couplings, chemical shift anisotropy, isotropic chemical shifts, and interactions with rf pulses:

\[
H(t) = H_D(t) + H_{\text{CSA}}(t) + H_{\text{ICS}} + H_{\text{RF}}(t)
\]  

(III.1)

#### A. Magnetic dipole-dipole coupling under MAS

For a pair of spins \(I_1\) and \(I_2\), the dipole-dipole coupling under MAS can be expressed as:

\[
H_D(t) = [A(\alpha,\beta) \cos(\omega_R t + \gamma) + B(\alpha,\beta) \sin(\omega_R t + \gamma) + C(\alpha,\beta) \cos(2\omega_R t + 2\gamma) + D(\alpha,\beta) \sin(2\omega_R t + 2\gamma)](3I_{1z}I_{2z} - I_1 \cdot I_2)
\]  

(III.2)

This is the “truncated” dipole-dipole coupling, i.e., the part for which \([\omega_0 I_z, H_D(t)] = 0\), where \(\omega_0\) is the NMR frequency (in rad/s) and \(\omega_0 I_z\) is the Zeeman interaction with the large external static field along \(z\) (which vanishes in the rotating frame). The full dipole-dipole coupling includes other terms (see the Appendix), which normally don’t affect high-field NMR spectra directly because they do not commute with the very strong Zeeman interaction, but do contribute to spin relaxation. Eq. (III.2) is one useful way to express \(H_D(t)\), but there are others (see Section VI, for example).

The MAS frequency is \(\omega_R = 2\pi / \tau_R\). The angles \(\alpha,\beta,\gamma\) are “Euler angles” that relate the orientation of a particular molecule within the MAS rotor to an axis system that is fixed with respect to the rotor:

\[
R_{z''}(\alpha)R_y''(\beta)R_{x''}(\gamma) \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix}
\]  

(III.3)

In Eq. (III.3), \(\{x',y',z'\}\) are the molecule-fixed axes and \(\{x'',y'',z''\}\) are the rotor-fixed axes. \(R_{z''}(\phi)\) and \(R_y''(\phi)\) are rotations of the axes about \(z''\) and \(y''\) by angle \(\phi\). These axis systems are depicted below:
Schematic depiction of an MAS rotor, showing rotor-fixed axes \( \{x'',y'',z''\} \) and randomly oriented molecules with molecule-fixed axes \( \{x',y',z'\} \). The two axis systems are related by rotations by Euler angles, as in Eq. (III.3), which are different for different molecules. The MAS rotor rotates about its \( z'' \) axis.

The coefficients \( A(\alpha,\beta), B(\alpha,\beta), C(\alpha,\beta), \) and \( D(\alpha,\beta) \) in Eq. (III.2) are proportional to \( \gamma_1^2/R^3 \), where \( \gamma_1 \) is the gyromagnetic ratio and \( R \) is the internuclear distance. We shall not worry about the detailed functional form of these coefficients in the analyses of recoupling sequences presented below. See the Appendix for a complete derivation of Eq. (III.2), including general expressions for these coefficients. The maximum value of the total coefficient of \( (3I_1I_2 - I_1 \cdot I_2) \) is \( \gamma_1^2 \hbar / R^3 \). For \(^{13}\text{C} \) spin pairs, this is \( 2\pi \times 7.59 \ \text{kHz} \) when \( R = 1.00 \ \text{Å} \).

Note that the dependence on the Euler angle \( \gamma \) always appears as \( \omega_R t + \gamma \). This is because molecules with different values of \( \gamma \) (but the same \( \alpha \) and \( \beta \)) differ in their orientations by a rotation about \( z'' \), which is the MAS rotation axis. So, as the sample spins, molecules with different values of \( \gamma \) are rotated into one another, thus having the same coefficient of \( (3I_1I_2 - I_1 \cdot I_2) \) at different values of \( t \).

Note that the time average of \( H_D(t) \) is zero under MAS. Note also that \( H_D(t) \) contains terms that oscillate at \( \omega_R \) and terms that oscillate at \( 2\omega_R \).

Finally, note that \( H_D(t) \) is a “zero-quantum operator”. This means that \( H_D(t) \) has non-zero matrix elements only between states that have the same total \( z \) component of angular momentum. For a system of two spin-\( 1/2 \) nuclei, the only non-zero matrix elements are

\[
<++ | (3I_1I_2 - I_1 \cdot I_2) | ++ > = -<-- | (3I_1I_2 - I_1 \cdot I_2) | --> = 1/2
\]  

(III.4a)
The dipole-dipole coupling for a static sample is obtained by setting $\omega_R$ to zero in Eq. (III.2). Recoupled dipole-dipole interactions generally have different orientation dependences than static couplings (i.e., different dependences on $\alpha, \beta, \gamma$), and can be zero-quantum, one-quantum, or two-quantum operators (or a mixture of these).

**B. Chemical shift anisotropy and isotropic chemical shift**

For one spin I,

$$H_{CSA}(t) = [A'(\alpha, \beta) \cos(\omega_R t + \gamma) + B'(\alpha, \beta) \sin(\omega_R t + \gamma)] I_z + C'(\alpha, \beta) \cos(2\omega_R t + 2\gamma) + D'(\alpha, \beta) \sin(2\omega_R t + 2\gamma)] I_z$$

$$H_{ICS} = \omega_I I_z$$

The isotropic chemical shift $\omega_I$ is defined here to be the time-independent part of the difference between the actual NMR frequency of spin I and the rf carrier frequency $\omega_{rf}$. Under MAS, the chemical shift anisotropy (CSA) has the same type of time-dependence as the dipole-dipole coupling (i.e., terms that oscillate at $\omega_R$ and $2\omega_R$), but the operator part is simply $I_z$. An important difference is that

$$e^{-iI_x\pi} H_D(t) e^{iI_x\pi} = H_D(t)$$

but

$$e^{-iI_x\pi} H_{CSA}(t) e^{iI_x\pi} = -H_{CSA}(t)$$

This allows chemical shifts and dipole-dipole couplings to be affected differently by pulse sequences, especially recoupling sequences.

**C. Radio-frequency pulses**

$$H_{RF}(t) = \omega_I(t)[I_x \cos(\phi(t)) + I_y \sin(\phi(t))]$$

The rf amplitude is $\omega_I(t)$. The rf phase is $\phi(t)$.

When a pulse sequence contains short pulses with amplitudes that greatly exceed the strengths of dipole-dipole and chemical shift interactions and the MAS frequency, the pulses can be treated as instantaneous rotations of spin angular momenta. This is the delta-function pulse limit. In this limit, the rotation (i.e., the evolution operator) produced by a pulse of length $t_p$ is the operator
R(\theta, \phi) = e^{-i(I_x \cos \phi + I_y \sin \phi)\theta}
= R_z(\phi)e^{-iI_x \theta}R_z(-\phi)
= R_z(\phi)R_x(\theta)R_z(-\phi)

(III.7)

where \theta = \omega t_p is the pulse flip angle.

In general, the net rotation produced by a pulse sequence alone (i.e., ignoring \(H_D(t), H_{CSA}(t),\) and \(H_{ICS}\)) is

\[U_{RF}(t) = \tilde{T} \exp\left\{-i \int_0^t dt' \omega_1(t') [I_x \cos \phi(t') + I_y \sin \phi(t')]\right\}
\]

(III.8)

If all pulses in a pulse sequence are phase-shifted by \(\Delta \phi\), then the net rotation becomes

\[U_{RF}(t; \Delta \phi) = \tilde{T} \exp\left\{-i \int_0^t dt' \omega_1(t') [I_x \cos \phi(t') + \Delta \phi + I_y \sin \phi(t') + \Delta \phi]\right\}
= \tilde{T} \exp\left\{-i e^{-iI_z \Delta \phi} \int_0^t dt' \omega_1(t') [I_x \cos \phi(t') + I_y \sin \phi(t')] e^{iI_z \Delta \phi}\right\}
= e^{-iI_z \Delta \phi} U_{RF}(t; 0) e^{iI_z \Delta \phi}
\]

(III.9)

Similarly, if we include all four Hamiltonian terms, the evolution operator for the pulse sequence is

\[U(t) = \tilde{T} \exp\left\{-i \int_0^t dt' [\omega_1(t') [I_x \cos \phi(t') + I_y \sin \phi(t')] + H_D(t') + H_{CSA}(t') + H_{ICS}]\right\}
\]

(III.10)

and a phase shift changes the evolution operator to

\[U(t; \Delta \phi) = \tilde{T} \exp\left\{-i \int_0^t dt' [\omega_1(t') [I_x \cos \phi(t') + \Delta \phi + I_y \sin \phi(t') + \Delta \phi] + H_D(t') + H_{CSA}(t') + H_{ICS}]\right\}
= \tilde{T} \exp\left\{-i e^{-iI_z \Delta \phi} \int_0^t dt' [\omega_1(t') [I_x \cos \phi(t') + I_y \sin \phi(t')] + H_D(t') + H_{CSA}(t') + H_{ICS}] e^{iI_z \Delta \phi}\right\}
= e^{-iI_z \Delta \phi} U(t; 0) e^{iI_z \Delta \phi}
\]

(III.11)

Eq. (III.11) is valid because \(H_D(t), H_{CSA}(t),\) and \(H_{ICS}\) all commute with \(I_z\). If this were not true (i.e., if we were not in the high-field limit), the effect of an overall rf phase shift could be more complicated.

Another useful operation is an rf phase reversal, meaning \(\phi(t) \rightarrow -\phi(t)\). The effect of a phase reversal is to change the evolution operator to
\[
U'(t) = \tilde{T} \exp \left\{ -i \int_0^t dt' [\omega(t') [I_x \cos(-\phi(t')) + I_y \sin(-\phi(t'))] + H_D(t') + H_{CSA}(t') + H_{ICS} \right\} \\
= \tilde{T} \exp \left\{ -i \int_0^t dt' [\omega(t') [I_x \cos(\phi(t')) - I_y \sin(\phi(t'))] + H_D(t') + H_{CSA}(t') + H_{ICS} \right\} \\
= \tilde{T} \exp \left\{ -i \int_0^t dt' e^{-i\pi I_x} [\omega(t') [I_x \cos(\phi(t')) + I_y \sin(\phi(t'))] + H_D(t') + H_{CSA}(t') + H_{ICS} \right\} e^{i\pi I_x} \\
= e^{-i\pi I_x} U''(t) e^{i\pi I_x} \\
\]

(III.12)

Thus, a phase reversal is equivalent to changing the sign of chemical shifts and rotating the resulting evolution operator \(U''(t)\) by 180° around \(x\).

**IV. Average Hamiltonian Theory in simple terms**

AHT [Haeberlen and Waugh, Phys. Rev. 175, 453 (1968)] is a mathematical formalism that allows us to analyze how pulse sequences affect internal spin interactions\(^1\,^2\). AHT is particularly useful in the derivation and analysis of pulse sequences that consist of a block of rf irradiation that is repeated many times. This is precisely the situation that arises in dipolar recoupling experiments. If the rf block has length \(\tau_c\) (called the cycle time), then AHT is applicable when the following conditions are met:

\[
\begin{align*}
H_{RF}(\tau_c + t) &= H_{RF}(t) \quad \text{(IV.1a)} \\
H_D(\tau_c + t) &= H_D(t) \quad \text{(IV.1b)} \\
H_{CSA}(\tau_c + t) &= H_{CSA}(t) \quad \text{(IV.1c)} \\
U_{RF}(\tau_c) &= 1 \quad \text{(IV.2)} \\
\| H_D \| \tau_c &< 1, \quad \| H_{CSA} \| \tau_c << 1, \quad \| H_{ICS} \| \tau_c << 1 \quad \text{(IV.3)}
\end{align*}
\]

Eqs. (IV.1) says that the rf pulse sequence is periodic and the internal spin interactions are also periodic. In recoupling sequences, this means \(\tau_c\) should be a multiple of \(\tau_R\). Eq. (IV.2) says that the net rotation produced by the rf block is zero (or sometimes a multiple of 2\(\pi\)). The rf block is then called a “cycle”. Eq. (IV.3) says that \(\tau_c\) is short enough that the dipole-dipole and chemical shift interactions can not produce a large change in the state of the spin system in one cycle. This allows a “perturbation theory” approach such as AHT to be employed, based on Eq. (II.9).

AHT depends on changing the picture in which we view the evolution of the spin system from the usual rotating frame (in which \(H_{RF}, H_D, H_{CSA},\) and \(H_{ICS}\) together determine the spin evolution) to a new frame of reference in which the rf pulses no longer appear directly. Instead,
the rf pulses cause additional time dependences in $H_D$, $H_{CSA}$, and $H_{ICS}$. This new frame of reference is called the interaction representation with respect to $H_{RF}$.

Mathematically, the interaction representation works as follows: If $U(t)$ is the evolution operator for the entire rotating frame Hamiltonian, we define a new evolution operator $\tilde{U}(t)$ that satisfies $U(t) = U_{RF}(t)\tilde{U}(t)$. Then we ask, “What is the new Hamiltonian that corresponds to $\tilde{U}(t)$?”

This is easily calculated, using the general relations $i \frac{d}{dt} U(t) = H(t)U(t)$ [see Eq. (I.4)] and $i \frac{d}{dt}[U(t)^{-1}] = -U(t)^{-1}H(t)$ [see Eqs (II.8) and recall that $U(t)$ is unitary and $H(t)$ is Hermitian; also, the adjoint of the number $i$ is $-i$].

$$i \frac{d}{dt} \tilde{U}(t) = i \frac{d}{dt}[U_{RF}(t)^{-1}U(t)]$$

$$= \left(i \frac{d}{dt}[U_{RF}(t)^{-1}]\right)U(t) + U_{RF}(t)^{-1}\left(i \frac{d}{dt} U(t)\right)$$

$$= -U_{RF}(t)^{-1}H_{RF}(t)U(t) + U_{RF}(t)^{-1}[H_{RF}(t) + H_D(t) + H_{CSA}(t) + H_{ICS}]U(t)$$

$$= U_{RF}(t)^{-1}[H_D(t) + H_{CSA}(t) + H_{ICS}]U_{RF}(t)\tilde{U}(t)$$

Therefore,

$$\tilde{H}(t) = \tilde{H}_D(t) + \tilde{H}_{CSA}(t) + \tilde{H}_{ICS} \quad \text{(IV.5)}$$

with

$$\tilde{H}_D(t) = U_{RF}(t)^{-1}H_D(t)U_{RF}(t) \quad \text{(IV.6a)}$$

$$\tilde{H}_{CSA}(t) = U_{RF}(t)^{-1}H_{CSA}(t)U_{RF}(t) \quad \text{(IV.6b)}$$

$$\tilde{H}_{ICS} = U_{RF}(t)^{-1}H_{ICS}U_{RF}(t) \quad \text{(IV.6c)}$$

So the dipole-dipole and chemical shift Hamiltonian terms in the interaction representation are the same as in the usual rotating frame, but with their spin operator parts rotated by $U_{RF}(t)^{-1}$. (Note that this rotation is the inverse of $U_{RF}(t)$, so the order of the pulses in a pulse sequence is reversed and the sign of the flip angles is changed. This is very important in AHT calculations.)

$U_{RF}(t)^{-1}$ acts on the spin operator parts of $H_D(t)$, $H_{CSA}(t)$, and $H_{ICS}(t)$, making these spin operator parts time-independent. In recoupling techniques, the time-dependence of the spin operator parts induced by the rf pulses interferes with the spatial time dependence from MAS, in general preventing $\tilde{H}_D(t)$ and/or $\tilde{H}_{CSA}(t)$ from averaging to zero.
Because of Eq. (IV.2), $\tilde{U}(\tau_c) = \tilde{U}(\tau_c)$. Because of Eq. (IV.1), $U(N\tau_c) = \tilde{U}(\tau_c)^N$. Because of Eq. (IV.3), we can approximate $\tilde{U}(\tau_c)$ by

$$\tilde{U}(\tau_c) \approx \exp\{-i\int_0^{\tau_c} dt\tilde{H}(t)\} = e^{-i\tilde{H}_{ave}\tau_c}$$

with $\tilde{H}_{ave} = \frac{1}{\tau_c} \int_0^{\tau_c} dt\tilde{H}(t)$. Therefore, as long as we care only about the state of the spin system at multiples of $\tau_c$ (and not in the middle of the rf blocks), then it is sufficient to calculate the average Hamiltonian in the interaction representation. To a good approximation, the NMR signals will be determined by $\tilde{H}_{ave}$ alone.

V. Homonuclear dipolar recoupling mechanisms

A. Delta-function pulse sequences

Consider the following simple pulse sequence, called DRAMA [see R. Tycko and G. Dabbagh, Chem. Phys. Lett. 173, 461 (1990)]:

How do we use AHT to calculate what this does to homonuclear dipole-dipole couplings and chemical shifts?

Because the sequence consists of delta-function pulses, $U_{RF}(t)$ is piecewise-constant:

$$U_{RF}(t) = \begin{cases} 1, & 0 < t < \tau_1 \\ e^{-iI_{1} \pi/2}, & \tau_1 < t < \tau_2 \\ 1, & \tau_2 < t < \tau_R \end{cases}$$

(V.1)

Abbreviating $A \cos(\omega_R t + \gamma) + B \sin(\omega_R t + \gamma) + C \cos(2\omega_R t + 2\gamma) + D \sin(2\omega_R t + 2\gamma)$ from Eq. (III.2) by $(A,B,C,D)$, the interaction representation Hamiltonians are
Now consider a longer DRAMA pulse sequence with additional 180° pulses:

\[ \tilde{H}_D(t) = \begin{cases} 
(A, B, C, D) \times (3I_z I_{z2} - I_1 \cdot I_2), & 0 < t < \tau_1 \\
(A, B, C, D) \times (3I_y I_{y2} - I_1 \cdot I_2), & \tau_1 < t < \tau_2 \\
(A, B, C, D) \times (3I_z I_{z2} - I_1 \cdot I_2), & \tau_2 < t < \tau_R 
\end{cases} \]  

(V.2)

\[ \tilde{H}_{CSA}(t) = \begin{cases} 
(A', B', C', D') \times I_z, & 0 < t < \tau_1 \\
(A', B', C', D') \times I_y, & \tau_1 < t < \tau_2 \\
(A', B', C', D') \times I_z, & \tau_2 < t < \tau_R 
\end{cases} \]  

(V.3a)

\[ \tilde{H}_{ICS}(t) = \begin{cases} 
\omega I_z, & 0 < t < \tau_1 \\
\omega I_y, & \tau_1 < t < \tau_2 \\
\omega I_z, & \tau_2 < t < \tau_R 
\end{cases} \]  

(V.3b)

The average Hamiltonians are

\[ \tilde{H}_{D,ave} = 3(I_y I_{y2} - I_z I_{z2}) \left\{ \frac{A}{2\pi} [\sin(\omega_R \tau_2 + \gamma) - \sin(\omega_R \tau_1 + \gamma)] - \frac{B}{2\pi} [\cos(\omega_R \tau_2 + \gamma) - \cos(\omega_R \tau_1 + \gamma)] \right. \\
+ \left. \frac{C}{4\pi} [\sin(2\omega_R \tau_2 + 2\gamma) - \sin(2\omega_R \tau_1 + 2\gamma)] - \frac{D}{4\pi} [\cos(2\omega_R \tau_2 + 2\gamma) - \cos(2\omega_R \tau_1 + 2\gamma)] \right\} \]  

(V.4)

\[ \tilde{H}_{CSA,ave} = (I_y - I_z) \left\{ \frac{A'}{2\pi} [\sin(\omega_R \tau_2 + \gamma) - \sin(\omega_R \tau_1 + \gamma)] - \frac{B'}{2\pi} [\cos(\omega_R \tau_2 + \gamma) - \cos(\omega_R \tau_1 + \gamma)] \right. \\
+ \left. \frac{C'}{4\pi} [\sin(2\omega_R \tau_2 + 2\gamma) - \sin(2\omega_R \tau_1 + 2\gamma)] - \frac{D'}{4\pi} [\cos(2\omega_R \tau_2 + 2\gamma) - \cos(2\omega_R \tau_1 + 2\gamma)] \right\} \]  

(V.5a)

\[ \tilde{H}_{ICS,ave} = \omega I [ (I_y - I_z) \frac{\tau_2 - \tau_1}{\tau_R} + I_z ] \]  

(V.5b)

So both the dipole-dipole coupling and the CSA are recoupled, and the isotropic chemical shift is altered. Note that only the $3I_z I_{z2}$ part of $H_D(t)$ contributes to the recoupled dipole-dipole Hamiltonian. This is a general rule, because the $I_1 \cdot I_2$ part is not affected by the rf pulses.
For this sequence

\[ U_{RF}(t) = \begin{cases} 
1.0 < t < \tau_1 \\
e^{-i\chi \pi/2}, \tau_1 < t < \tau_2 \\
1, \tau_2 < t < \tau_R \\
e^{-i\chi \pi}, \tau_R < t < \tau_R + \tau_1 \\
e^{-i\chi 3\pi/2}, \tau_R + \tau_1 < t < \tau_R + \tau_2 \\
e^{-i\chi \pi}, \tau_R + \tau_2 < t < 2\tau_R 
\end{cases} \quad (V.6) \]

\[ \tilde{H}_D(t) = \begin{cases} 
(A,B,C,D) \times (3I_{z1}I_{z2} - I_1 \cdot I_2), 0 < t < \tau_1 \\
(A,B,C,D) \times (3I_{y1}I_{y2} - I_1 \cdot I_2), \tau_1 < t < \tau_2 \\
(A,B,C,D) \times (3I_{z1}I_{z2} - I_1 \cdot I_2), \tau_2 < t < \tau_R \\
(A,B,C,D) \times (3I_{z1}I_{z2} - I_1 \cdot I_2), \tau_R < t < \tau_R + \tau_1 \\
(A,B,C,D) \times (3I_{y1}I_{y2} - I_1 \cdot I_2), \tau_R + \tau_1 < t < \tau_R + \tau_2 \\
(A,B,C,D) \times (3I_{z1}I_{z2} - I_1 \cdot I_2), \tau_R + \tau_2 < t < 2\tau_R 
\end{cases} \quad (V.7) \]

\[ \tilde{H}_{CSA}(t) = \begin{cases} 
(A',B',C',D') \times I_z, 0 < t < \tau_1 \\
(A',B',C',D') \times I_y, \tau_1 < t < \tau_2 \\
(A',B',C',D') \times I_z, \tau_2 < t < \tau_R \\
-(A',B',C',D') \times I_z, \tau_R < t < \tau_R + \tau_1 \\
-(A',B',C',D') \times I_y, \tau_R + \tau_1 < t < \tau_R + \tau_2 \\
-(A',B',C',D') \times I_z, \tau_R + \tau_2 < t < 2\tau_R 
\end{cases} \quad (V.8a) \]

\[ \tilde{H}_{ICS}(t) = \begin{cases} 
\omega_1 I_z, 0 < t < \tau_1 \\
\omega_1 I_y, \tau_1 < t < \tau_2 \\
\omega_1 I_z, \tau_2 < t < \tau_R \\
-\omega_1 I_z, \tau_R < t < \tau_R + \tau_1 \\
-\omega_1 I_y, \tau_R + \tau_1 < t < \tau_R + \tau_2 \\
-\omega_1 I_z, \tau_R + \tau_2 < t < 2\tau_R 
\end{cases} \quad (V.8b) \]
Now, $\tilde{H}_{D,\text{ave}}$ is the same as before (because $\tilde{H}_D(t)$ is not affected by the additional 180° pulses), but $\tilde{H}_{\text{CSA,ave}} = \tilde{H}_{\text{ICS,ave}} = 0$ (because the 180° pulses change the signs of $\tilde{H}_{\text{CSA}}(t)$ and $\tilde{H}_{\text{ICS}}(t)$ in the second rotor period). Dipole-dipole couplings are now selectively recoupled.

Through the dependence on $\alpha$, $\beta$, and $\gamma$, $\tilde{H}_{D,\text{ave}}$ depends on molecular orientation in the MAS rotor. Dipolar lineshapes are then powder patterns. The lineshape depends on $\tau_2 - \tau_1$, because the A, B, C, and D terms have different relative magnitudes for different values of $\tau_2 - \tau_1$. In the limit that $(\tau_2 - \tau_1)/\tau_R \ll 1$, the lineshape resembles the Pake doublet pattern of a static sample for a two-spin system. Note that the operator part of $\tilde{H}_{D,\text{ave}}$ under DRAMA is different from the operator part of $H_D(t)$. Under the DRAMA sequences depicted above, $\tilde{H}_{D,\text{ave}}$ contains both zero-quantum and double-quantum terms.

Simulated dipolar powder patterns for two-spin $^{13}$C system with maximum splitting = 1.5 kHz ($R = 2.48 \ \text{Å}$)

Experimental dipolar powder patterns (Fourier transform with respect to $t_1$) for $^{13}$CH$_3_2$C(OH)SO$_3$Na powder, for which $R = 2.51 \ \text{Å}$.
B. Continuous rf irradiation

Consider the following pulse sequence, called 2Q-HORROR [see N.C. Nielsen, H. Bildsoe, H.J. Jakobsen, and M.H. Levitt, J. Chem. Phys. 101, 1805 (1994)]:

In other words, the cycle here is a 90°-360°-90° sequence, with delta-function 90° pulses and a very long, weak 360° pulse. For this sequence,

$$U_{RF}(t) = e^{-i\chi \omega_R t} e^{-i\gamma t/2}$$

$$= e^{-i\chi \omega_R t/2} e^{-i\gamma t/2}$$ (V.9)

for $0 < t < 2\tau_R$. The interaction representation Hamiltonians are then

$$\tilde{H}_D(t) = (A,B,C,D) \times [3(-I_x \cos \frac{\omega_R t}{2} + I_y \sin \frac{\omega_R t}{2})(-I_x \cos \frac{\omega_R t}{2} + I_y \sin \frac{\omega_R t}{2})]$$

$$= (A,B,C,D) \times [3(I_x^2 + I_y^2) - 2I_x I_y)(-I_x \cos \frac{\omega_R t}{2} + I_y \sin \frac{\omega_R t}{2})]$$

$$= (A,B,C,D) \times \left[ \frac{3}{2} (I_x^2 + I_y^2) + 2i(I_x I_y + I_y I_x) + 3I_x I_y \sin \omega_R t + (I_x I_y + I_y I_x) \cos \omega_R t) - I_1 \cdot I_2 \right]$$ (V.10)

$$\tilde{H}_{CSA}(t) = (A',B',C',D') \times (-I_x \cos \frac{\omega_R t}{2} + I_y \sin \frac{\omega_R t}{2})$$ (V.11a)

$$\tilde{H}_{ICS}(t) = \omega_I (-I_x \cos \frac{\omega_R t}{2} + I_y \sin \frac{\omega_R t}{2})$$ (V.11b)

Eq. (V.10) makes use of the identities $\cos^2 \theta = (1 + \cos 2\theta)/2$ and $\sin^2 \theta = (1 - \cos 2\theta)/2$, as well as $I_z = I_x + iI_y$. Although $\tilde{H}_D(t)$ contains both double-quantum and zero-quantum operator terms, only the double-quantum terms oscillate in time. Therefore, only the double-quantum terms are recoupled. Using the relations

$$\int_0^{2\tau_R} dt \cos \frac{k\omega_R t}{2} \cos \frac{n\omega_R t}{2} = \tau_R \delta_{k,n},$$
\[ \int_0^{2\tau} dt \sin \left( \frac{k \omega_R t}{2} \right) \sin \left( \frac{n \omega_R t}{2} \right) = \tau R \delta_{k,n}, \text{ and } \int_0^{2\tau} dt \sin \left( \frac{k \omega_R t}{2} \cos \frac{n \omega_R t}{2} \right) = 0 \] for integers \( k \) and \( n \), it is straightforward to show that \( \tilde{H}_{\text{CSA,ave}} = \tilde{H}_{\text{ICS,ave}} = 0 \) and that

\[ \tilde{H}_{\text{D,ave}} = \frac{3}{8} [(I_{+1}I_{+2} + I_{-1}I_{-2})(A \cos \gamma + B \sin \gamma) + i(I_{+1}I_{+2} - I_{-1}I_{-2})(-A \sin \gamma + B \cos \gamma)] \]  

(V.12)

Thus, the 2Q-HORROR sequence creates a pure double-quantum recoupled Hamiltonian (assuming that the AHT approximation is valid and that the pulses are perfect). The average Hamiltonian contains two double-quantum terms, whose magnitudes depend on the Euler angles \( \alpha, \beta, \gamma \). Interestingly, the overall magnitude of \( \tilde{H}_{\text{D,ave}} \) is independent of the \( \gamma \) angle. Recoupling sequences with this property are called “\( \gamma \)-encoded”. This property causes the dipolar powder pattern lineshape under 2Q-HORROR and other \( \gamma \)-encoded sequences to have two sharp horns (see below), which means that the signal decay under \( \tilde{H}_{\text{D,ave}} \) is strongly oscillatory. This is good for quantitative measurements of internuclear distances, and also for double-quantum filtering efficiencies.

Simulated and experimental 2Q-HORROR data for a \( ^{13}\text{C}^{13}\text{C} \) pair with \( R \approx 1.54 \) Å [from Nielsen et al, J. Chem. Phys. 101, 1805 (1994)].

The cycle time is $4\tau_R$, there is one $180^\circ$ pulse in each rotor period, and the pulse length is a significant fraction of the rotor period. The rf amplitude during each pulse is $\omega_1 = \frac{\pi}{\tau_p}$. For this pulse sequence,

$U_{RF}(t) = \begin{cases} 
  e^{-i\pi I_x t/\tau_p}, & 0 < t < \tau_p \\
  e^{-i\pi I_x \tau_p}, & \tau_p < t < \tau_R \\
  e^{-i\pi I_y (t-\tau_R)/\tau_p} e^{-i\pi I_x \tau_R} e^{-i\pi I_x \tau_p}, & \tau_R < t < \tau_R + \tau_p \\
  e^{-i\pi I_y} e^{-i\pi I_x \tau_R} e^{-i\pi I_x \tau_p} t < 2\tau_R \\
  e^{-i\pi I_y (2\tau_R-t)/\tau_p} e^{-i\pi I_x \tau_R} e^{-i\pi I_x \tau_p}, & 2\tau_R < t < 2\tau_R + \tau_p \\
  e^{-i\pi I_x} e^{-i\pi I_y} e^{-i\pi I_x}, & 2\tau_R + \tau_p < t < 3\tau_R \\
  e^{-i\pi I_y (3\tau_R-t)/\tau_p} e^{-i\pi I_x} e^{-i\pi I_x} e^{-i\pi I_y}, & 3\tau_R < t < 3\tau_R + \tau_p \\
  e^{-i\pi I_y} e^{-i\pi I_x} e^{-i\pi I_y} e^{-i\pi I_x}, & 3\tau_R + \tau_p < t < 4\tau_R 
\end{cases}$

Using the identity $e^{-i\pi I_y} e^{-i\pi I_x} = e^{i\pi I_z}$, Eq. (V.13) can be simplified:
Ignoring the $I_1I_2$ term (which is not recoupled, as explained above), the interaction-representation dipole-dipole Hamiltonian is then

\[
U_{RF}(t) = \begin{cases} 
  e^{-i\pi I_x t/\tau_p}, & 0 < t < \tau_p \\
  e^{-i\pi I_x}, & \tau_p < t < \tau_R \\
  e^{-i\pi I_y (t-\tau_R)/\tau_p} e^{-i\pi I_x}, & \tau_R < t < \tau_R + \tau_p \\
  e^{i\pi I_x}, & \tau_R + \tau_p < t < 2\tau_R \\
  e^{-i\pi I_x (t-2\tau_R)/\tau_p} e^{i\pi I_x}, & 2\tau_R < t < 2\tau_R + \tau_p \\
  e^{-i\pi I_y}, & 2\tau_R + \tau_p < t < 3\tau_R \\
  e^{-i\pi I_y (t-3\tau_R)/\tau_p} e^{-i\pi I_x}, & 3\tau_R < t < 3\tau_R + \tau_p \\
  1, & 3\tau_R + \tau_p < t < 4\tau_R 
\end{cases}
\]

(V.14)

This can be rewritten as

\[
\tilde{H}_D(t) = \begin{cases} 
  (A,B,C,D) \times [3(I_{x2} \cos \frac{\pi I}{\tau_p} + I_{y2} \sin \frac{\pi I}{\tau_p})(I_{x2} \cos \frac{\pi I}{\tau_p} + I_{y2} \sin \frac{\pi I}{\tau_p})], 0 < t < \tau_p \\
  (A,B,C,D) \times (3I_{x2} I_{y2}), \tau_p < t < \tau_R \\
  (A,B,C,D) \times [3(I_{x2} \cos \frac{\pi (t-\tau_R)}{\tau_p} + I_{y2} \sin \frac{\pi (t-\tau_R)}{\tau_p})(I_{x2} \cos \frac{\pi (t-\tau_R)}{\tau_p} + I_{y2} \sin \frac{\pi (t-\tau_R)}{\tau_p})], \tau_R < t < \tau_R + \tau_p \\
  (A,B,C,D) \times (3I_{x2} I_{y2}), \tau_R + \tau_p < t < 2\tau_R \\
  (A,B,C,D) \times [3(I_{x2} \cos \frac{\pi (t-2\tau_R)}{\tau_p} - I_{y2} \sin \frac{\pi (t-2\tau_R)}{\tau_p})(I_{x2} \cos \frac{\pi (t-2\tau_R)}{\tau_p} - I_{y2} \sin \frac{\pi (t-2\tau_R)}{\tau_p})], 2\tau_R < t < 2\tau_R + \tau_p \\
  (A,B,C,D) \times (3I_{x2} I_{y2}), 2\tau_R + \tau_p < t < 3\tau_R \\
  (A,B,C,D) \times [3(I_{x2} \cos \frac{\pi (t-3\tau_R)}{\tau_p} - I_{y2} \sin \frac{\pi (t-3\tau_R)}{\tau_p})(I_{x2} \cos \frac{\pi (t-3\tau_R)}{\tau_p} - I_{y2} \sin \frac{\pi (t-3\tau_R)}{\tau_p})], 3\tau_R < t < 3\tau_R + \tau_p \\
  (A,B,C,D) \times (3I_{x2} I_{y2}), 3\tau_R + \tau_p < t < 4\tau_R 
\end{cases}
\]

(V.15a)

Note that the signs of $I_1I_2+I_3I_2$ and $I_1I_2+I_1I_2$ are reversed in the third and fourth rotor periods, relative to the first and second rotor periods. This is a consequence of the choice of...
phases in the fpRFDR sequence [called XY-4 phases\(^7\)], and it causes these single-quantum terms to cancel out in the average Hamiltonian. Evaluating the integrals in the average Hamiltonian, we find (omitting many intermediate steps)

\[
\tilde{H}_{D,\text{ave}} = \frac{1}{4\tau_R} \left\{ 4 \int_{\tau_p}^{\tau} dt \tilde{H}_D(t) + \int_{\tau_x}^{\tau} dt \tilde{H}_D(t) + \int_{\tau_x}^{\tau + \tau_p} dt \tilde{H}_D(t) + \int_{2\tau_x}^{2\tau_x + \tau_p} dt \tilde{H}_D(t) + \int_{3\tau_x}^{3\tau_x + \tau_p} dt \tilde{H}_D(t) \right\}
\]

\[
= \frac{1}{4\tau_R} \left\{ 4 \int_{\tau_p}^{\tau} dt (A, B, C, D) \times (3I_x I_{x2}) + 4 \int_{0}^{\tau_p} dt (A, B, C, D) \times (3I_x I_{x2} \cos \frac{\pi t}{\tau_p}) \right\}
\]

\[
+ 2 \int_{0}^{\tau_p} dt (A, B, C, D) \times (3I_x I_{x2} + 3I_y I_{y2}) \sin^2 \frac{\pi t}{\tau_p} \}
\]

\[
= \left\{ \frac{3\omega_1^2}{2\pi(\omega_R^2 - 4\omega_1^2)} \left[ \sin(\omega_R \tau_p + \gamma) - \sin \gamma \right] A - \frac{3\omega_1^2}{2\pi(\omega_R^2 - 4\omega_1^2)} \left[ \cos(\omega_R \tau_p + \gamma) - \cos \gamma \right] B \right. 
\]

\[
\left. + \frac{3\omega_1^2}{16\pi(\omega_R^2 - \omega_1^2)} \left[ \sin(2\omega_R \tau_p + 2\gamma) - \sin 2\gamma \right] C - \frac{3\omega_1^2}{16\pi(\omega_R^2 - \omega_1^2)} \left[ \cos(2\omega_R \tau_p + 2\gamma) - \cos 2\gamma \right] D \right\} 
\]

\[
= [I_x I_{x2} - I_1 \cdot I_2] 
\]

(V.16)

Miraculously (or as a consequence of symmetry, as described below), the average dipole-dipole Hamiltonian under the fpRFDR sequence is a zero-quantum operator with the same operator form as the dipole-dipole coupling in a non-spinning sample. This has useful consequences in certain applications, for example by allowing ideas that were originally developed for NMR of static solids to be applied in MAS experiments\(^8,9\).

Under fpRFDR, it is also true that \(\tilde{H}_{\text{CSA,ave}} = \tilde{H}_{\text{ICS,ave}} = 0\).

\(\omega_1\) in Eq. (V.16) is the rf amplitude during the 180° pulses. Note that \(\tilde{H}_{D,\text{ave}}\) vanishes as \(\omega_1 \to \infty\) and \(\tau_p \to 0\) (i.e., in the delta-function pulse limit). As shown below, a different recoupling mechanism, leading to a different average dipole-dipole Hamiltonian, comes into play when the coupled spins have large chemical shift differences. This chemical-shift-driven recoupling mechanism does not disappear in the delta-function pulse limit.
D. Chemical-shift-driven recoupling

1. Rotational resonance

Now consider the case where two dipole-coupled spins have a large difference in their isotropic chemical shifts. Ignore chemical shift anisotropy for now. The nuclear spin Hamiltonian under MAS is then

\[ H(t) = \omega_{\text{I}} I_{z1} + \omega_{\text{I}2} I_{z2} + H_D(t) \]

\[ = \frac{1}{2} (\omega_{\text{I}} + \omega_{\text{I}2})(I_{z1} + I_{z2}) + \frac{1}{2} (\omega_{\text{I}} - \omega_{\text{I}2})(I_{z1} - I_{z2}) + H_D(t) \]

\[ = \frac{1}{2} \Sigma(I_{z1} + I_{z2}) + \frac{1}{2} \Delta(I_{z1} - I_{z2}) + H_D(t) \]  \hspace{1cm} (V.17)

where \( \Sigma \) and \( \Delta \) are the sum and difference of the two chemical shifts (actually, resonance offsets). Now go into an interaction representation with respect to the chemical shift terms. If \( U(t) \) is the evolution operator for \( H(t) \), this interaction representation is defined by

\[ U(t) = U_{\text{ICS}}(t) \tilde{U}(t) \] \hspace{1cm} (V.18a)

\[ U_{\text{ICS}}(t) = \exp\{-i[\frac{1}{2} \Sigma(I_{z1} + I_{z2}) + \frac{1}{2} \Delta(I_{z1} - I_{z2})]t\} \]

\[ = \exp[-\frac{1}{2} \Sigma(I_{z1} + I_{z2})t] \exp[-\frac{1}{2} \Delta(I_{z1} - I_{z2})t] \] \hspace{1cm} (V.18b)

\[ \tilde{U}(t) = \tilde{T} \exp\{-i \int_0^t dt' \tilde{H}_D(t')\} \] \hspace{1cm} (V.18c)

\[ \tilde{H}_D(t) = U_{\text{ICS}}(t)^{-1} H_D(t) U_{\text{ICS}}(t) \]

\[ = \exp[\frac{1}{2} \Delta(I_{z1} - I_{z2})t] H_D(t) \exp[-\frac{1}{2} \Delta(I_{z1} - I_{z2})t] \]

\[ = (A, B, C, D) \times \exp[\frac{1}{2} \Delta(I_{z1} - I_{z2})t][2I_{z1}I_{z2} - \frac{1}{2} (I_{z1} + I_{z2} + I_{z1} - I_{z2})] \exp[-\frac{1}{2} \Delta(I_{z1} - I_{z2})t] \]

\[ = (A, B, C, D) \times (2I_{z1}I_{z2}) \]

\[ - \frac{1}{2} (A, B, C, D) \times \exp[\frac{1}{2} \Delta(I_{z1} - I_{z2})t][I_{z1} + I_{z1} - I_{z1} + I_{z1} - I_{z1} - I_{z1}] \exp[-\frac{1}{2} \Delta(I_{z1} - I_{z2})t] \] \hspace{1cm} (V.19)

Eq. (V.19) uses the facts that \( [(I_{z1} + I_{z2}), H_D(t)] = 0 \), so the \( \Sigma \) part of the chemical shift does not affect \( \tilde{H}_D(t) \), and that \( [(I_{z1} - I_{z2}), I_{z1}I_{z2}] = 0 \), so the \( I_{z1}I_{z2} \) part of \( H_D(t) \) is not affected by the chemical shifts. Also, Eq. (V.19) uses the identity \( I_1 \cdot I_2 = I_{z1}I_{z2} + \frac{1}{2} (I_{z1} - I_{z2} + I_{z1} + I_{z2}) \). Now, using the identity \( e^{i\phi} I_\pm e^{-i\phi} = e^{\pm i\phi} I_\pm \), Eq. (V.19) becomes

\[ \tilde{H}_D(t) = (A, B, C, D) \times (2I_{z1}I_{z2}) - \frac{1}{2} (A, B, C, D) \times (e^{i\Delta t} I_{z1}I_{z2} + e^{-i\Delta t} I_{z1}I_{z2}) \]

\[ = (A, B, C, D) \times (2I_{z1}I_{z2}) - \frac{1}{2} (A, B, C, D) \times [(\cos \Delta t + i \sin \Delta t)I_{z1}I_{z2} + (\cos \Delta t - i \sin \Delta t)I_{z1}I_{z2}] \]
Eq. (V.20) shows that the $I_1 I_2$ part of the dipole-dipole coupling is not recoupled by the chemical shift difference, but the “flip-flop” part can be recoupled if $|\Delta| = \omega_R$ or $|\Delta| = 2\omega_R$. These are the “n = 1” and “n = 2” rotational resonance conditions\(^{10-14}\). At the rotational resonance conditions, $\tilde{H}_D(t)$ is periodic with period $\tau_R$ and AHT can be applied. The average dipole-dipole Hamiltonian at rotational resonance is

$$\tilde{H}_{D,\text{ave}} = -\frac{1}{4}[(A + iB)e^{-i\gamma\delta_{1,n}} + (C + iD)e^{-2i\gamma\delta_{2,n}}] I_{+1} I_{-2} - \frac{1}{4}[(A - iB)e^{i\gamma\delta_{1,n}} + (C - iD)e^{2i\gamma\delta_{2,n}}] I_{-1} I_{+2}$$

(V.21)

for $n = 1$ or $n = 2$. Note that this is a zero-quantum operator, but it is not the same as the zero-quantum operator created by the fpRFDR sequence.

In a system with many $^{13}$C-labeled sites, rotational resonance allows pairs of spins with particular chemical shift differences to be recoupled selectively\(^{15,16}\), as shown below. However, unless the MAS frequency is varied during the pulse sequence, the couplings can not be switched on and off. Therefore, other approaches to frequency-selective homonuclear dipolar recoupling that employ rf pulses and do not depend on being exactly on rotational resonance have been developed by several groups\(^{17-22}\).

\[\text{13C NMR spectra of U-15N, 13C-alanine powder, recorded at 100.8 MHz, with MAS frequencies indicated by dashed lines. At the rotational resonance conditions, the recoupled lines become dipolar powder patterns, while other lines remain sharp. Close to rotational resonance conditions (C and D), the main NMR lines of strongly coupled pairs exhibit apparent shifts on the order of 0.5 ppm, which can complicate accurate measurements of chemical shifts in uniformly labeled samples.}\]
2. Radio-Frequency-Driven Recoupling

Consider the Hamiltonian in Eq. (V.17), but with an additional $H_{RF}(t)$ term that corresponds to the following pulse sequence, with $m$ being an arbitrary positive integer:

This sequence, called SEDRA\(^{23}\) or more commonly RFDR\(^{6,24}\), can be analyzed by first transforming the Hamiltonian into an interaction representation with respect to $H_{RF}(t)$, and then into an interaction representation with respect to the chemical shifts. Following the same principles as used above for other recoupling sequences, the Hamiltonian in the interaction representation with respect to $H_{RF}(t)$ is

$$
\tilde{H}(t) = \begin{cases}
\frac{1}{2} \Sigma (I_{z1} + I_{z2}) + \frac{1}{2} \Delta (I_{z1} - I_{z2}) + H_D(t), & 0 < t < t_c/4 \\
- \frac{1}{2} \Sigma (I_{z1} + I_{z2}) - \frac{1}{2} \Delta (I_{z1} - I_{z2}) + H_D(t), & t_c/4 < t < 3t_c/4 \\
\frac{1}{2} \Sigma (I_{z1} + I_{z2}) + \frac{1}{2} \Delta (I_{z1} - I_{z2}) + H_D(t), & 3t_c/4 < t < t_c 
\end{cases}
$$

(V.21)

$H_D(t)$ is not affected directly by the delta-function 180° pulses, but the chemical shifts change sign between the two 180° pulses. Therefore, the isotropic chemical shifts now appear to be time-dependent. In the second interaction representation, the dipole-dipole coupling becomes

$$
\tilde{H}_D(t) = \begin{cases}
\exp\left[\frac{i}{2} \Delta (I_{z1} - I_{z2}) t\right] H_D(t) \exp\left[-\frac{i}{2} \Delta (I_{z1} - I_{z2}) t\right], & 0 < t < t_c/4 \\
\exp\left[\frac{i}{2} \Delta (I_{z1} - I_{z2}) (\frac{\tau_c}{2} - t)\right] H_D(t) \exp\left[-\frac{i}{2} \Delta (I_{z1} - I_{z2}) (\frac{\tau_c}{2} - t)\right], & t_c/4 < t < 3t_c/4 \\
\exp\left[\frac{i}{2} \Delta (I_{z1} - I_{z2}) (t - \tau_c)\right] H_D(t) \exp\left[-\frac{i}{2} \Delta (I_{z1} - I_{z2}) (t - \tau_c)\right], & 3t_c/4 < t < t_c 
\end{cases}
$$

(V.22)

Ignoring the $I_{z1}I_{z2}$ part of $H_D(t)$, which as shown above is not recoupled, Eq. (V.22) can be written as

$$
\tilde{H}_D(t) = \begin{cases}
- \frac{1}{2} (A, B, C, D) \times [e^{i\Delta t} I_{+1} I_{-2} + e^{-i\Delta t} I_{-1} I_{+2}], & 0 < t < t_c/4 \\
- \frac{1}{2} (A, B, C, D) \times [e^{i\Delta (\tau_c/2-t)} I_{+1} I_{-2} + e^{-i\Delta (\tau_c/2-t)} I_{-1} I_{+2}], & t_c/4 < t < 3t_c/4 \\
- \frac{1}{2} (A, B, C, D) \times [e^{i\Delta (t-\tau_c)} I_{+1} I_{-2} + e^{-i\Delta (t-\tau_c)} I_{-1} I_{+2}], & 3t_c/4 < t < t_c 
\end{cases}
$$

(V.23)
The average Hamiltonian is then
\[
\tilde{H}_{D,\text{ave}} = \left[ (-1)^m \frac{\Delta \sin(m\Delta \tau_R/2)}{m \tau_R (\omega_R^2 - \Delta^2)} (A \cos \gamma + B \sin \gamma) + \frac{\Delta \sin(m\Delta \tau_R/2)}{m \tau_R (4\omega_R^2 - \Delta^2)} (C \cos 2\gamma + D \sin 2\gamma) \right] (I_{+1}I_{-2} + I_{-1}I_{+2})
\]

Note that the average dipole-dipole Hamiltonian, evaluated in the double interaction representation described above, is non-zero for nearly all values of the chemical shift difference \(\Delta\). This is because the 180° pulses, spaced \(m \tau_R\) apart, force the flip-flop term in \(\tilde{H}_D(t)\) to be periodic with period \(2m \tau_R\). For nearly all values of \(\Delta\), \(\tilde{H}_D(t)\) has non-zero Fourier components at \(\omega_R\) and/or \(2\omega_R\). However, \(\tilde{H}_{D,\text{ave}} \to 0\) as \(\Delta \to 0\). Thus, the recoupling mechanism for RFDR in the delta-function pulse limit (i.e., when the 180° pulses are very short compared with \(\tau_R\)) is qualitatively different from the recoupling mechanism in the finite-pulse limit (i.e., when the 180° pulses occupy a significant fraction of the rotor period).

In actual experiments, the phases of the 180° pulses are usually chosen to follow an XY-4 or high XY-n phase pattern, because XY-n phase patterns compensate for rf inhomogeneity, resonance offsets, and other imperfections in the 180° pulses. This makes the RFDR technique (and the fpRFDR version) quite robust and useful in many experimental situations.

VI. Symmetry principles for recoupling sequences

A. Levitt’s “C” sequences

Malcolm Levitt and his colleagues have developed an approach to the development of recoupling sequences that relies on general symmetry properties of pulse sequences, which lead to “selection rules” that reveal which types of interactions can be recoupled by a sequence with a given symmetry. Sequences belonging to two distinct symmetry classes have been described. The first class includes “C” sequences, comprised of rf blocks (called C elements) that produce no net rotation of spin angular momenta. The general form for a C sequence is:

\[
\begin{align*}
C_0 & \quad C_\phi & \quad C_{2\phi} & \quad \vdots & \quad C_{(N-2)\phi} & \quad C_{(N-1)\phi} \\
\end{align*}
\]

In other words, the C sequence contains \(N\) repetitions of the C element, with overall rf phase shifts that increase in units of \(\phi\), and with a total cycle time of \(n \tau_R\). The phase
increment satisfies $\phi = 2\pi \nu / N$. $N$, $n$, and $\nu$ are positive integers. The symmetry is represented by the symbol $CN_n^\nu$.

To analyze the effect of a $CN_n^\nu$ sequence with AHT, one considers a general nuclear spin Hamiltonian under MAS that is a sum of terms of the form $H_{m\lambda,0}(t) = A_m e^{i\omega_R t}T_{\lambda,0}$ in the rotating frame [i.e., before transforming to an interaction representation with respect to $H_{RF}(t)$]. $A_m$ is a function of the Euler angles $\alpha, \beta, \gamma$ discussed above. $m$ is -2, -1, 1, or 2, and $\lambda$ is another positive integer.

$T_{\lambda,0}$ is the "element of an irreducible tensor operator of rank $\lambda$" that commutes with the total spin angular momentum $I_z$. Without going into the details of irreducible tensor operators, this means $T_{\lambda,0}$ is an operator that is a member of a set of $2\lambda + 1$ operators $\{T_{\lambda,\mu}\}$, with $\mu$ being an integer that satisfies $-\lambda \leq \mu \leq \lambda$. For dipole-dipole couplings, $\lambda = 2$ and the relevant set of operators is

$$T_{2\pm 2} = \frac{1}{2} I_{\pm 1} I_{\pm 2}$$
$$T_{2\pm 1} = \frac{\mp 1}{2} (I_{\pm 1} I_{\pm 2} + I_{\pm 1} I_{\pm 2})$$
$$T_{20} = \frac{1}{\sqrt{6}} (3I_{\pm 1} I_{\pm 2} - I_1 \cdot I_2)$$

Thus, $T_{2\mu}$ is a $\mu$-quantum operator. For isotropic and anisotropic chemical shifts, the relevant operators have $\lambda = 1$.

Important properties of irreducible tensor operators include:

$$e^{iI_z \theta} T_{\lambda,\mu} e^{-iI_z \theta} = e^{i\mu \theta} T_{\lambda,\mu}$$
$$e^{-iI_x \pi} T_{\lambda,\mu} e^{iI_x \pi} = (-1)^\lambda T_{\lambda,-\mu}$$
$$T_{\lambda,\mu}^\dagger = (-1)^\mu T_{\lambda,-\mu}$$

Elements of the set of operators $\{T_{\lambda,\mu}\}$ are transformed into one another by rotations of spin angular momentum (i.e., by rf pulses in NMR experiments). Therefore, in the interaction representation with respect to the first C element, the nuclear spin Hamiltonian is a sum of terms of the form $\tilde{H}_{m\lambda,\mu}(t) = \tilde{A}_{m\lambda,\mu}(t) e^{i\omega_R t} T_{\lambda,\mu}$ in the interval $0 < t < n\tau_R/N$. There are $4 \times (2\lambda + 1)$ such terms. The interaction representation Hamiltonian for the $k^{th}$ C element must then be a sum of terms of the form

$$\tilde{H}_{m\lambda,\mu}(t) = \tilde{A}_{m\lambda,\mu}(t) e^{i\omega_R t} t (e^{-iI_z (k-1)\phi} T_{\lambda,\mu} e^{iI_z (k-1)\phi})$$

in the interval $(k-1)n\tau_R/N < t < kn\tau_R/N$, taking into account the effect of the overall rf phase shift as in Eqs. (III.8-III.11). The average Hamiltonian for the $k^{th}$ C element will then be a sum of terms of the form
\[ \tilde{H}_{m,\lambda,\mu,\text{ave}}(k) = \frac{N}{n\tau_R} \int_{(k-1)n\tau_R}^{kn\tau_R} \int_0^{n\tau_R} \mathcal{H}_{m,\lambda,\mu}(t) \, dt \]

\[ = T_{\lambda,\mu} \frac{N}{n\tau_R} e^{-i\mu(k-1)\phi} e^{im\omega R (k-1)n\tau_R} \int_0^{n\tau_R} \int_0^{n\tau_R} \mathcal{A}_{m,\lambda,\mu}(t) e^{im\omega R t} \, dt \eqno (VI.4) \]

Eq. (VI.4) makes use of Eq. (VI.2a) and the fact that \( \tilde{A}_{m,\lambda,\mu}(t) \) is periodic, with period equal to \( n\tau_R/N \) (the length of one C element). The total average Hamiltonian, for the entire cycle time \( n\tau_R \), is obtained by summing over contributions from all C elements. The total average Hamiltonian will then contain \( 4 \times (2\lambda + 1) \) terms of the form

\[ \tilde{H}_{m,\lambda,\mu,\text{ave}} = T_{\lambda,\mu} \frac{N}{n\tau_R} \sum_{k=1}^{N} \left\{ e^{-i\mu(k-1)\phi} e^{im\omega R (k-1)n\tau_R} \int_0^{n\tau_R} \int_0^{n\tau_R} \mathcal{A}_{m,\lambda,\mu}(t) e^{im\omega R t} \, dt \right\} \]

\[ = T_{\lambda,\mu} \frac{N}{n\tau_R} \int_0^{n\tau_R} \int_0^{n\tau_R} \mathcal{A}_{m,\lambda,\mu}(t) e^{im\omega R t} \sum_{k=1}^{N} \left\{ e^{-i\mu(k-1)\phi} e^{im\omega R (k-1)n\tau_R} \right\} \]

\[ = T_{\lambda,\mu} \frac{N}{n\tau_R} \int_0^{n\tau_R} \int_0^{n\tau_R} \mathcal{A}_{m,\lambda,\mu}(t) e^{im\omega R t} \sum_{k=1}^{N} \left\{ e^{-i2\pi(k-1)(\mu\nu - mn)/N} \right\} \eqno (VI.5) \]

For such a term to be non-zero, the sum over \( k \) must be non-zero. But it turns out that the following relation is always true, for any positive integer \( N \):

\[ \sum_{k=1}^{N} e^{-i2\pi(k-1)q/N} = \begin{cases} N, & q = NZ \\ 0, & q \neq NZ \end{cases} \eqno (VI.6) \]

where \( Z \) is some other integer. So the quantity \( \mu\nu - mn \) must be zero or another integer multiple of \( N \) for the average Hamiltonian under a C sequence to contain non-zero \( \mu \)-quantum terms that arise from MAS-induced oscillations at frequency \( m\omega_R \). This is the selection rule for \( CN_{\mu,\nu} \) sequences.

The \( C7 \) and POST-\( C7 \) recoupling sequences are good examples. For these sequences, \( N = 7 \), \( n = 2 \), and \( \nu = 1 \), which imply the selection rule that \( \mu - 2m = 0, 7, 14, \) etc. Thus, terms with \( \mu = 2 \) and \( m = 1 \) or \( \mu = -2 \) and \( m = -1 \) are recoupled (corresponding to double-quantum dipolar recoupling). Terms with \( \mu = 0 \) and \( 1 \) are not recoupled, corresponding to the absence of CSA recoupling and the absence of both zero-quantum and one-quantum dipolar recoupling. (Recall that \( m \) has only the values \( \pm 1 \) and \( \pm 2 \), but not 0, under MAS.) \( C7 \) and POST-\( C7 \) differ in the choice of the C element itself, which is better compensated for resonance offsets in the POST-\( C7 \) case.
**B. Levitt’s “R” sequences**

The second symmetry class considered by Levitt and coworkers includes the "R" sequences\(^{29,30}\), which have the general form

\[
2n\tau_R/N \quad \begin{array}{cccc}
R_\phi & R'_\phi & R_\phi & R'_\phi \\
\end{array}
\]

The sequence consists of \(N\) repetitions of an "R element" in a cycle time \(n\tau_R\). \(N\) is an even integer. The rf pulses in the R element produce a net rotation by 180° around \(x\). The \(R_\phi\) version alternates with the \(R'_\phi\) version. For the \(R_\phi\) version, all rf pulses in the R element are phase-shifted by \(\phi = \pi v / N\). For the \(R'_\phi\) version, all rf pulses in the R element are first reversed in sign, then phase-shifted by \(-\phi\). The symmetry is represented by the symbol \(RN_n\).

Analysis of R sequences is similar to analysis of C sequences, but the fact that one R element produces a net 180° rotation means that \(T_{\lambda\mu}\) and \(T_{\lambda'\mu}\) terms must be treated together [see Eq. (VI.2b)]. For the Hamiltonian to be Hermitian, these must occur in the interaction representation as terms of the form

\[
\sum c_{\lambda'\mu}(t)T_{\lambda'\mu} + (\lambda')\bar{c}_{\lambda'\mu}(t)\bar{T}_{\lambda'\mu} + (-1)^{\lambda'}\bar{A}_{\lambda'\mu}(t)e^{-i\omega_\lambda t} - T_{\lambda'\mu} \quad \text{[so that]} \quad \bar{H}_{\lambda'\mu}(t) = H_{\lambda'\mu}(t)^\dagger; \text{ see Eq. (VI.2c)}.
\]

Considering only one \(m,\lambda,\mu\) combination initially, the evolution operator for the R element, starting at \(t = 0\), is

\[
U_R = \bar{T}\exp\left\{-i\int_{0}^{n\tau_R/N} dt \left[ H_{RF}(t) + (A_m e^{i\omega_\mu t} + A_m^* e^{-i\omega_\mu t})T_{\lambda\mu} \right] \right\} \quad (VI.7a)
\]

Then, in the AHT approximation and considering only one \(m,\lambda,\mu\) combination,

\[
U_R \approx e^{-i\pi\lambda x} \exp\left\{-i\int_{0}^{n\tau_R/N} dt \left( \bar{A}_{\lambda\mu}(t)e^{i\omega_\mu t} - (\lambda')\bar{A}_{\lambda'\mu}(t)e^{-i\omega_\mu t} - T_{\lambda\mu} \right) \right\} \quad (VI.7b)
\]

In going from Eq. (VI.7a) to Eq. (VI.7b), the fact that \(H_{RF}(t)\) produces a net rotation by 180° around \(x\) has been used. In the interaction representation with respect to \(H_{RF}(t)\), \(T_{\lambda,0}\) becomes a sum of terms of the form \(c_{\lambda\mu}(t)T_{\lambda\mu} + (\lambda')\bar{c}_{\lambda\mu}(t)^*T_{\lambda'\mu}\). In Eq. (VI.7b), \(\bar{A}_{m\lambda\mu}(t) \equiv A_m c_{\lambda\mu}(t)\).
Terms proportional to $e^{-im\sigma t}T_{\lambda,\mu}$ and $e^{im\sigma t}T_{\lambda,-\mu}$ are not shown explicitly, but of course are also present.

The corresponding equations for the phase-reversed element $R'$, starting at $t = 0$, are [see Eq. (III.12)]

$$U_{R'} = T \exp \left\{ -i \sum_{n}^{N} \frac{\rho}{n} \int_{0}^{\tau} dt \left[ e^{-i\pi x H_{RF}(t)} e^{i\pi x} + (A_{m} e^{im\sigma t} + A_{m}' e^{-im\sigma t}) T_{\lambda,0} \right] \right\}$$  \hspace{1cm} (VI.8a)

$$U_{R'} \approx e^{-i\pi x} \left[ \exp \left\{ -i \sum_{n}^{N} \frac{\rho}{n} \int_{0}^{\tau} dt (\tilde{A}_{m\lambda}(t) e^{im\sigma t}T_{\lambda,\mu} + (-1)^{\mu} \tilde{A}_{m\lambda}(t) e^{-im\sigma t}T_{\lambda,-\mu}) \right\} \right] e^{i\pi x}$$  \hspace{1cm} (VI.8b)

Eqs. (VI.7) and (VI.8) show that $U_{R}$ and $U_{R'}$ differ by exchange of $T_{\lambda,\mu}$ and $T_{\lambda,-\mu}$ in the interaction representation.

Including rotations about z to account for the phase shifts, the evolution operator for the first $R_{S} R'_{S}$ pair is

$$U_{0} = e^{i\phi} e^{-i\pi x} \left[ \exp \left\{ -i \sum_{n}^{N} \frac{\rho}{n} \int_{0}^{\tau} dt (\tilde{A}_{m\lambda}(t) e^{im\sigma t}T_{\lambda,\mu} + (-1)^{\mu} \tilde{A}_{m\lambda}(t) e^{-im\sigma t}T_{\lambda,\mu}) \right\} \right] e^{-i\pi x}$$

$$= e^{i\phi} e^{-i\pi x} \left[ \exp \left\{ -i \sum_{n}^{N} \frac{\rho}{n} \int_{0}^{\tau} dt (\tilde{A}_{m\lambda}(t) e^{im\sigma t}T_{\lambda,\mu} + (-1)^{\mu} \tilde{A}_{m\lambda}(t) e^{-im\sigma t}T_{\lambda,\mu}) \right\} \right] e^{i\pi x}$$

$$= e^{i\phi} e^{-i\pi x} \left[ \exp \left\{ -i \sum_{n}^{N} \frac{\rho}{n} \int_{0}^{\tau} dt (\tilde{A}_{m\lambda}(t) e^{im\sigma t}T_{\lambda,\mu} + (-1)^{\mu} \tilde{A}_{m\lambda}(t) e^{-im\sigma t}T_{\lambda,\mu}) \right\} \right] e^{i\pi x}$$

The total evolution operator is

$$U_{\text{total}} = e^{i2N\pi x} \prod_{k=0}^{(N/2)-1} U_{R}(k) \tilde{U}_{R}(k)$$  \hspace{1cm} (VI.10)

with $\tilde{U}_{R}(k)$ and $\tilde{U}_{R'}(k)$ defined by
\[ \tilde{U}_R (k) = \exp \left\{ -i \int \frac{n \tau_R}{N} dt [\tilde{A}_{m\lambda,\mu}(t) e^{i 4\pi m k / N} e^{i m \omega_R t} e^{-i (4k+1) \mu \phi} T_{\lambda,\mu} + (-1)^{\mu} \tilde{A}_{m\lambda,\mu}(t) * e^{-i 4\pi m k / N} e^{i m \omega_R t} e^{i (4k+1) \mu \phi} T_{\lambda,\mu} ] \right\} \] (VI.11a)

\[ \tilde{U}_R'(k) = \exp \left\{ -i \int \frac{n \tau_R}{N} dt (-1)^{\lambda} [\tilde{A}_{m\lambda,\mu}(t) e^{i 2\pi m(2k+1) / N} e^{i m \omega_R t} e^{i (4k+3) \mu \phi} T_{\lambda,\mu} + (-1)^{\mu} \tilde{A}_{m\lambda,\mu}(t) * e^{-i 2\pi m(2k+1) / N} e^{i m \omega_R t} e^{i (4k+3) \mu \phi} T_{\lambda,\mu} ] \right\} \] (VI.11b)

Note that \( 2N\phi \) in Eq. (VI.10) is a multiple of \( 2\pi \), so the operator \( e^{i 2Nz\phi} \) has no effect. The average Hamiltonian for the entire R sequence is obtained by summing the exponents in \( U_R(k) \) and \( U_R'(k) \) over all values of \( k \) and dividing by \( n \tau_R \). Therefore, the coefficient of \( T_{\lambda,\mu} \) in the average Hamiltonian arising from MAS-induced oscillations at \( m \omega_R \) is proportional to

\[ \int_0^{n \tau_R / N} dt [\tilde{A}_{m\lambda,\mu}(t) e^{i m \omega_R t} e^{-i \pi \mu \nu / N} \left\{ \sum_{k=0}^{(N/2)-1} \exp[i 4\pi (mn - \mu \nu)k / N] + (-1)^{\lambda} \sum_{k=0}^{(N/2)-1} \exp[i 4\pi (mn - \mu \nu)(k+1/2) / N] \right\} \] (VI.12)

Eq. (VI.12) shows that if \( \lambda \) is even, the coefficient of \( T_{\lambda,\mu} \) is zero (i.e., no recoupling) unless \( mn - \mu \nu \) is an even multiple of \( N/2 \). If \( \lambda \) is odd, the coefficient of \( T_{\lambda,\mu} \) is zero unless \( mn - \mu \nu \) is an odd multiple of \( N/2 \). These are the selection rules for \( R N_n^\nu \) sequences.

Many examples of \( R N_n^\nu \) recoupling sequences have been reported. The fpRFDR sequence described above is a very simple example, for which \( n = 4, \ N = 4, \) and \( \nu = 1 \). The symmetry selection rules indicate that dipole-dipole couplings \( (\lambda = 2) \) can be recoupled in a zero-quantum \( (\mu = 0) \) form, with \( |m| = 1 \) or \( |m| = 2 \). Chemical shifts \( (\lambda = 1; |\mu| = 0 \ or \ 1) \) can not be recoupled. This is in agreement with the detailed calculations described above.

**C. Cyclic time displacement symmetry and constant-time recoupling**

Another useful symmetry property of recoupling sequences involves their behavior when all pulses are cyclically displaced in time within the cycle time \( \tau_c = n \tau_R \). In the picture below, a block of pulses (or delays) of length \( \tau_1 \), called \( P_1 \), is displaced by \( \tau_2 \), causing the remaining block \( P_2 \) to move from the end to the beginning of the cycle:
What is the effect of this cyclic displacement on a recoupled Hamiltonian? If the rotations produced by rf pulse blocks $P_1$ and $P_2$ are $U_1(t)$ and $U_2(t)$, with time $t$ measured from the beginning of each block, then the total rotation before the cyclic displacement is $U_{RF}(t)$:

$$U_{RF}(t) = \begin{cases} 
U_1(t), & 0 < t < \tau_1 \\
U_2(t - \tau_1)U_1(\tau_1), & \tau_1 < t < n\tau_R 
\end{cases} \quad (VI.13)$$

The total rotation after the cyclic displacement is $U_{CD}(t)$:

$$U_{CD}(t) = \begin{cases} 
U_2(t), & 0 < t < \tau_2 \\
U_1(t - \tau_2)U_2(\tau_2), & \tau_2 < t < n\tau_R 
\end{cases} \quad (VI.14)$$

In the interaction representation with respect to the original pulse sequence, a Hamiltonian term of the form $H_{\lambda,m}(t) = A_{\lambda,m}e^{i\text{mod}tT_{\lambda,0}}$ under MAS becomes (recalling that $\tau_1 + \tau_2 = n\tau_R$)

$$\tilde{H}_{\lambda,m}(t) = \begin{cases} 
A_{\lambda,m}e^{i\text{mod}t}U_1(t)^{-1}T_{\lambda,0}U_1(t), & 0 < t < \tau_1 \\
A_{\lambda,m}e^{i\text{mod}t}U_1(\tau_1)^{-1}U_2(t - \tau_1)^{-1}T_{\lambda,0}U_2(t - \tau_1)U_1(\tau_1), & \tau_1 < t < n\tau_R 
\end{cases} \quad (VI.15)$$

with $t' = t + \tau_1$. In the interaction representation with respect to the cyclically displaced pulse sequence, the same Hamiltonian term becomes
\[
\hat{H}_{\lambda m}(t) = \begin{cases} 
A_{\lambda m} e^{i \phi R} t U_2(t)^{-1} T_\lambda U_2(t), & 0 < t < \tau_2 \\
A_{\lambda m} e^{i \phi R} t U_2(\tau_2)^{-1} U_1(t - \tau_2)^{-1} T_\lambda U_1(t - \tau_2) U_2(\tau_2), & \tau_2 < t < n \tau_R \\
A_{\lambda m} e^{-i \phi R} t \tau_2 e^{i \phi R} t'' U_2(\tau_2)^{-1} U_1(t'')^{-1} T_\lambda U_1(t'') U_2(\tau_2), & 0 < t'' < \tau_1
\end{cases}
\] (VI.16)

with \( t'' = t + \tau_2 \). In both cases, the average Hamiltonian is the integral of the interaction representation Hamiltonian over time from 0 to \( n \tau_R \), divided by \( n \tau_R \). According to Eqs. (VI.15) and (VI.16), the integral in both cases is the sum of two integrals, over time intervals of length \( \tau_1 \) and \( \tau_2 \). Recalling that \( e^{i \phi R} t \tau_1 e^{i \phi R} t \tau_2 = 1 \) and \( U_2(\tau_2) U_1(\tau_1) = 1 \), it can be shown that the integrands for the cyclically displaced pulse sequence are equal to the integrands for the original pulse sequence after rotation by \( U_2(\tau_2)^{-1} = U_1(\tau_1) \) and multiplication by \( e^{i \phi R} t \tau_2 \). Thus,

\[
\hat{H}_{\lambda m, \text{ave}} = e^{i \phi R} t \tau_2 U_2(\tau_2)^{-1} \hat{H}_{\lambda m, \text{ave}} U_2(\tau_2) 
\] (VI.17)

Eq. (VI.17) summarizes the effect of a cyclic time displacement on the average Hamiltonian for an arbitrary recoupling sequence.

Why is this useful? As an example, consider a general recoupling sequence that ends in two periods of length \( \tau_R/3 \). During these final two periods, either no pulses are applied or the applied pulses produce a net rotation of \( 2\pi \). For such a sequence, two successive cyclic displacements by \( \tau_R/3 \) multiply the average Hamiltonian by \( e^{i 2 m \pi / 3} \) and \( e^{i 4 m \pi / 3} \). For \( m = \pm 1 \) and \( m = \pm 2 \), the total average Hamiltonian for the pulse sequence obtained by concatenating the original sequence with the two displaced versions will be zero, because \( 1 + e^{i 2 m \pi / 3} + e^{i 4 m \pi / 3} = 0 \). This provides a simple means of creating a “constant-time” dipolar recoupling technique, as shown below using cyclically displaced versions of the fpRFDR sequence:
Construction of a constant-time dipolar recoupling sequence from the fpRFDR sequence. During the “k₂” period, dipolar recoupling by the A, B, and C blocks cancels due to Eq. (VI.17). Only the “k₃” period has a net recoupling effect. Thus, by decrementing k₂ and incrementing k₃ while keeping k₂ + k₃ constant, the effective recoupling period τD’ can be increased from 0 to 12k₁(k₂ + k₃)τR. For all values of τD’, the total fpRFDR period is 12k₁(k₂ + k₃)τR and the total number of pulses is constant. Thus, signal decay due to spin relaxation, incomplete proton decoupling, and pulse imperfections is minimized. The dependence of NMR signals on τD’ is due primarily to dipole-dipole couplings rather than these extraneous effects, allowing the recoupling data to be analyzed in a quantitative manner. [from J. Chem. Phys. 126, 064506 (2007)]
Measurements of backbone $^{15}$N-$^{15}$N distances (which constrain the $\psi$ torsion angle) in a model helical peptide in lyophilized form using the PITHIRDS-CT recoupling technique. Both $^{15}$N-detected data (b) and $^{13}$C$_\alpha$-detected data (a) are shown, along with numerical simulations (d). [from J. Chem. Phys. 126, 064506 (2007)]
Appendix: Derivation of time-dependent dipole-dipole coupling under MAS

In angular frequency units and in a molecule-fixed frame (i.e., in an axis system that has any specific orientation relative to the molecular structure or crystallite unit cell), the full dipole-dipole coupling can be written as

\[ H_D = \frac{3 \gamma_1^2 \hbar}{R^3} \sum_{m=-2}^{2} (-1)^m Y_{2m} T_{2-m} \]  

(A.1)

with

\[ T_{2\pm2} = \frac{1}{2} I_{\pm1} I_{\pm2} \]
\[ T_{2\pm1} = \mp \frac{1}{2} (I_z I_{\pm2} + I_{\pm1} I_{z2}) \]  

(A.2)
\[ T_{20} = \frac{1}{\sqrt{6}} (3 I_z I_{z2} - I_1 \cdot I_2) \]
\[ Y_{2\pm2} = \frac{1}{2} \sin^2 \theta \cos \pm 2i \phi \]
\[ Y_{2\pm1} = \mp \sin \theta \cos \pm i \phi \]  

(A.3)
\[ Y_{20} = \frac{1}{\sqrt{6}} (3 \cos^2 \theta - 1) \]

In Eq. (A.3), \( \theta \) and \( \phi \) are angles that specify the direction of the internuclear vector in the molecule-fixed frame. It is important to realize that the \( Y_{2m} \) functions are simply (complex) numbers for a given pair of coupled nuclei. These numbers do not change when the transformations described below are carried out. It is the \( T_{2m} \) operators that change under these transformations.

Suppose the molecule-fixed frame (with axes \( x', y', z' \) as in Section III.A) is related to a MAS-rotor-fixed frame (with axes \( x'', y'', z'' \)) by Euler angles \( \alpha \beta \gamma \). The spinning axis is taken to be \( z'' \). \( x'' \) and \( y'' \) are perpendicular to the spinning axis. In other words, the \( x', y', z' \) axes are transformed to the \( x'', y'', z'' \) axes by three consecutive rotations: first, a rotation about \( z' \) by \( \alpha \); second, a rotation about the intermediate \( y \) axis by \( \beta \); third, a rotation about the \( z'' \) axis by \( \gamma \). Then the irreducible tensor operator components are transformed according to

\[ T_{2m} \rightarrow \sum_{m=-2}^{2} D_{m' m}^{(2)} (-\gamma, -\beta, -\alpha) T_{2m'} \]  

(A.4a)

with

\[ D_{m' m}^{(2)} (\alpha, \beta, \gamma) = e^{-im' \gamma} d_{m' m}^{(2)} (\beta) e^{-im \alpha} \]  

(A.4b)

and
\[ d_{00}^{(2)}(\beta) = (3\cos^2\beta - 1)/2 \]
\[ d_{0\pm 1}^{(2)}(\beta) = -d_{\pm 10}^{(2)}(\beta) = \mp \sqrt{6}/2 \sin \beta \cos \beta \]
\[ d_{0\pm 2}^{(2)}(\beta) = d_{\pm 20}^{(2)}(\beta) = \sqrt{6}/4 \sin^2 \beta \]
\[ d_{1\pm 1}^{(2)}(\beta) = \frac{1}{2} (1 \pm \cos \beta)(2 \cos \beta \mp 1) \]
\[ d_{-1\pm 1}^{(2)}(\beta) = \frac{1}{2} (1 \mp \cos \beta)(2 \cos \beta \pm 1) \]
\[ d_{1\pm 2}^{(2)}(\beta) = \pm \frac{1}{2} \sin \beta (1 \pm \cos \beta) \]
\[ d_{-1\pm 2}^{(2)}(\beta) = \pm \frac{1}{2} \sin \beta (1 \mp \cos \beta) \]
\[ d_{2\pm 1}^{(2)}(\beta) = -\frac{1}{2} \sin \beta (1 \pm \cos \beta) \]
\[ d_{-2\pm 1}^{(2)}(\beta) = \frac{1}{2} \sin \beta (1 \mp \cos \beta) \]
\[ d_{2\pm 2}^{(2)}(\beta) = \frac{1}{4} (1 \pm \cos \beta)^2 \]
\[ d_{-2\pm 2}^{(2)}(\beta) = \frac{1}{4} (1 \mp \cos \beta)^2 \]

\{ D_{m'm}^{(s)}(\alpha, \beta, \gamma) \} are Wigner rotation matrix elements, equal to \{ \langle sm'| e^{-iS_\alpha} e^{-iS_\beta} e^{-iS_\gamma} | sm \rangle \} for a spin-s particle, with m and m' being quantum numbers for \( S_z \). \{ d_{m'm}^{(s)}(\beta) \} are reduced rotation matrix elements, equal to \{ \langle sm'| e^{-i\beta} | sm \rangle \}.

The order and signs of the Euler angles may look strange in Eq. (A.4a). This is because Eq. (A.4a) indicates how an irreducible tensor operator defined in the initial axis system appears in the final axis system. Eq. (A.4a) does not indicate what happens when the rotation \( R(\alpha, \beta, \gamma) = e^{-iS_\alpha} e^{-iS_\beta} e^{-iS_\gamma} \) is applied to the irreducible tensor operator itself. The former case can be called a "passive rotation", and the latter case an "active rotation". The distinction can be confusing, leading to a variety of errors, which may or may not be significant, depending on the whether the signs of angles are important, etc. The following article is a useful review of rotations, Euler angles, irreducible tensors, spherical harmonics, and Wigner rotation matrices: A.A. Wolf, "Rotation Operators", Am. J. Phys. 37, 531-536 (1969).

In Eq. (A.1), the \( T_{2m} \) operators are functions of spin angular momentum components in the molecule-fixed frame. When written in terms of spin angular momentum components in the rotor-fixed frame, \( H_D \) becomes

\[ H_D = \frac{3\gamma_i^2 \hbar}{R^3} \sum_{m,m'=2} (-1)^m Y_{2m}(\beta) e^{-im\alpha} d_{m'-m}^{(2)}(-\beta) e^{-im\alpha} T_{2m'} \]

In Eq. (A.6), the \( T_{2m} \) operators are functions of spin angular momentum components in the rotor-fixed frame. Next, the rotor fixed frame is transformed to the laboratory-fixed frame (with axes...
x, y, z) by a time-dependent rotation about z" by \( \omega_R t \) that makes y" perpendicular to z and coincident with y (because z" is the spinning axis and because we define t = 0 to be a time when y" and y coincide), followed by a rotation about y by the magic angle \( \theta_M \) that brings z" to z. Under these rotations,

\[
T_{2m'} \rightarrow \sum_{m''=-2}^{2} D_{m'm''}^{(2)} (0, -\theta_M, \omega_R t) T_{2m''} \tag{A.7}
\]

\[
H_D = \frac{3\gamma_1^2}{R^3} \sum_{m,m',m''=-2}^{2} (-1)^m Y_{2m} e^{im \gamma} d_{m'-m}^{(2)} (-\beta) e^{-im \alpha} d_{m''m'}^{(2)} (-\theta_M) e^{im \alpha \theta_M} T_{2m''} \tag{A.8}
\]

\[
H_D = \frac{3\gamma_1^2}{R^3} \sum_{m,m',m''=-2}^{2} (-1)^m Y_{2m} d_{m'-m}^{(2)} (-\beta) e^{-im \alpha} d_{m''m'}^{(2)} (-\theta_M) e^{im \alpha \theta_M} T_{2m''} \tag{A.9}
\]

\( H_D \) in Eq. (A.8) is the full dipole-dipole coupling as it appears in the laboratory frame under MAS, written in terms of the angles \( \theta \) and \( \phi \) that specify the direction of the internuclear vector relative to the molecule-fixed axes and the angles \( \alpha, \beta, \) and \( \gamma \) that specify the orientation of the molecule in the rotor. The \( T_{2m''} \) operators in Eq. (A.8) are functions of spin angular momentum components in the laboratory frame.

In high field, terms in Eq. (A.8) with \( m'' \neq 0 \) are truncated by the much larger Zeeman interaction with the external magnetic field. In other words, only the \( m'' = 0 \) term affects the frequencies and intensities of NMR signals or affects coherent spin dynamics in high field. Furthermore, at the magic angle, the \( m' = 0 \) term vanishes because \( d_{00}^{(2)} (\pm \theta_M) = 0 \). This what makes the magic angle so magical. Then the remaining terms oscillate at \( \omega_R \) and \( 2\omega_R \), and average to zero unless recoupling techniques are employed.

\[
H_D \rightarrow \frac{3\gamma_1^2}{R^3} \sum_{m,m',m''=-2, m'=0}^{2} (-1)^m Y_{2m} d_{m'-m}^{(2)} (-\beta) e^{-im \alpha} d_{0m''}^{(2)} (-\theta_M) e^{im \alpha \theta_M} T_{20} \tag{A.9}
\]

Explicit expressions for the A, B, C, and D coefficients in Eq. (III.2) and the \( A_m \) coefficients used in Section VI can be derived from Eq. (A.9). In particular, if

\[
H_D(t) = \sum_{m=-2}^{2} A_m e^{im (\omega_R t + \gamma)} \times (3 I_{21} I_{22} - I_1 \cdot I_2), \quad \text{then}
\]
\[ A_{\pm 2} = \frac{\gamma_1^2 \hbar}{2R^3} \sum_{m=2}^{2} (-1)^m Y_{2m} d_{\pm 2, -m} (2) (-\beta)e^{-i\alpha} \]

\[ = \frac{\gamma_1^2 \hbar}{16R^3} [\sin^2 \theta e^{2i\phi} (1 \mp \cos \beta)^2 e^{-2i\alpha} + \sin^2 \theta e^{-2i\phi} (1 \pm \cos \beta)^2 e^{2i\alpha}] \quad (A.10a) \]

\[ \pm 2 \sin 2\theta e^{i\phi} \sin \beta (1 \mp \cos \beta)e^{-i\alpha} \mp 2 \sin 2\theta e^{-i\phi} \sin \beta (1 \pm \cos \beta)e^{i\alpha} \]

\[ + 2(3 \cos^2 \theta - 1) \sin^2 \beta \]

\[ A_{\mp 1} = \mp \frac{\gamma_1^2 \hbar}{\sqrt{2R^3}} \sum_{m=-2}^{2} (-1)^m Y_{2m} d_{\pm 1, -m} (2) (-\beta)e^{-i\alpha} \]

\[ = \mp \frac{\gamma_1^2 \hbar}{4\sqrt{2R^3}} [\sin^2 \theta e^{2i\phi} \sin \beta (1 \mp \cos \beta)e^{-2i\alpha} - \sin^2 \theta e^{-2i\phi} \sin \beta (1 \pm \cos \beta)e^{2i\alpha}] \quad (A.10b) \]

\[ - \sin 2\theta e^{i\phi} \sin \beta (1 \mp \cos \beta)(2 \cos \beta \pm 1)e^{-i\alpha} + \sin 2\theta e^{-i\phi} \sin \beta (1 \pm \cos \beta)(2 \cos \beta \mp 1)e^{i\alpha} \]

\[ \mp (3 \cos^2 \theta - 1) \sin 2\beta \]

In the special case of a two-spin system, we can take \( \theta = 0 \), which implies \( A_{\pm 2} = \gamma_1^2 \hbar \sin^2 \beta / 4R^3 \) and \( A_{\mp 1} = \gamma_1^2 \hbar \sin 2\beta / 2\sqrt{2R^3} \). The coefficients in Eq. (III.2) are given by \( A = 2\Re(A_1) \), \( B = -2\Im(A_1) \), \( C = 2\Re(A_2) \), and \( D = 2\Im(A_2) \).
References


