

Lecture #1: Hamiltonians, Density Operators, and Time Evolution

1. NMR Hamiltonians

1.1 Zeeman interaction

The largest interaction in NMR is the Zeeman interaction, which describes the preferential alignment of the nuclear magnetic dipolar moment $\vec{M} = \gamma\hbar\hat{I}$ along the magnetic field \vec{B}_0 :

$$\hat{H}_0 = -\vec{M} \cdot \vec{B}_0 = -\gamma\hbar\hat{I} \cdot \vec{B}_0 = -\gamma\hbar B_0 \hat{I}_z = \hbar\omega_0 \hat{I}_z$$

All nuclear spins of the same type (γ) experience the same Zeeman interaction, irrespective of the electronic environment around each individual spin. Therefore the Zeeman interaction does not contain information on chemical structure. But the Zeeman interaction is so much larger than all internal nuclear spin interactions that it defines the quantization axis for the local spin interactions.

1.2. Chemical shift interaction

Nuclear spins also experience smaller interactions in its local environments. The chemical shift interaction arises from the shielding of the nuclear spins from the external magnetic field by the surrounding electrons. Because of the electronic shielding, nuclei experience a weaker magnetic field. Depending on the bonding, different nuclei have different electron densities around them, thus the amount of shielding differs. This gives rise to different NMR frequencies.

In general, the electron density distribution around a nucleus is not spherical, so chemical shift interaction is orientation-dependent (anisotropic), with some direction more shielded than others. In isotropic solution, molecules undergo fast tumbling in all directions (isotropic), so the anisotropic chemical shift is averaged to the same value, σ_{iso} , for all directions.

The chemical shielding Hamiltonian is:

$$\begin{aligned} \hat{H}_{cs} &\equiv \gamma\hbar\hat{I} \cdot \sigma \cdot \vec{B}_0 = \gamma\hbar \begin{pmatrix} \hat{I}_x & \hat{I}_y & \hat{I}_z \end{pmatrix} \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}^{LF} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} \\ &\Rightarrow \hat{H}_{cs} = \gamma\hbar B_0 (\hat{I}_x \sigma_{xz}^{LF} + \hat{I}_y \sigma_{yz}^{LF} + \hat{I}_z \sigma_{zz}^{LF}) \end{aligned}$$

Truncation of Hamiltonians

The chemical shift interaction is much weaker than the Zeeman interaction, i.e. $\sigma_{ij} \ll 1$. Under this condition, time-independent perturbation theory indicates that \hat{H}_{cs} is truncated by the large Zeeman interaction to give only spin operators that commute with \hat{H}_0 . This means only spin operators that commute with \hat{I}_z survive in the chemical shift interaction. These commuting terms include 1, \hat{I}_z , $\hat{I} \cdot \hat{I}$, and their products.

Truncation simplifies the full chemical shift Hamiltonian $\hat{H}_{cs} = \gamma\hbar B_0 (\hat{I}_x \sigma_{xz}^{LF} + \hat{I}_y \sigma_{yz}^{LF} + \hat{I}_z \sigma_{zz}^{LF})$ to:

$$\hat{H}_{cs}^{(0)} = \gamma\hbar B_0 \hat{I}_z \sigma_{zz}^{LF}$$

Combining Zeeman interaction with the chemical shift interaction, we obtain

$$\hat{H}_0 + \hat{H}_{cs}^{(0)} = \hbar\omega_0 (1 - \sigma_{zz}^{LF}) \hat{I}_z$$

So the observed precession frequency is: $\omega = \omega_0 (1 - \sigma_{zz}^{LF})$.

1.3. Dipolar interaction

General form:
$$\hat{H}_D = \hat{I}^j \cdot D \cdot \hat{I}^k = -\frac{\mu_0}{4\pi} \hbar^2 \gamma_j \gamma_k \frac{1}{r^3} \left[3(\hat{I}^j \cdot \vec{e}_{jk})(\hat{I}^k \cdot \vec{e}_{jk}) - \hat{I}^j \cdot \hat{I}^k \right]$$

The scalar products lead to a lengthier expression:

$$\hat{H}_D = -\hbar\omega_D \left[3 \begin{pmatrix} \hat{I}_x^j & \hat{I}_y^j & \hat{I}_z^j \end{pmatrix} \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix} \cdot \begin{pmatrix} \hat{I}_x^k & \hat{I}_y^k & \hat{I}_z^k \end{pmatrix} \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix} - (\hat{I}_x^j \hat{I}_x^k + \hat{I}_y^j \hat{I}_y^k + \hat{I}_z^j \hat{I}_z^k) \right]$$

This Hamiltonian contains two-spin operators such as $\hat{I}_x^j \hat{I}_x^k$, $\hat{I}_y^j \hat{I}_y^k$, $\hat{I}_z^j \hat{I}_z^k$, $\hat{I}_x^j \hat{I}_y^k$, etc, with their corresponding trigonometric terms.

To proceed further, we distinguish between heteronuclear and homonuclear dipolar coupling.

Heteronuclear I-S dipolar coupling: $\omega_I - \omega_S \gg \omega_D$

Two spins with different gyromagnetic ratios have large sum and difference chemical shifts:

$$\hat{H}_0 = \hbar\omega_I \hat{I}_z + \hbar\omega_S \hat{S}_z = \frac{1}{2}\hbar(\omega_I + \omega_S)(\hat{I}_z + \hat{S}_z) + \frac{1}{2}\hbar(\omega_I - \omega_S)(\hat{I}_z - \hat{S}_z)$$

Here both $\omega_I \pm \omega_S \gg \omega_D$. So truncation will retain only with \hat{H}_D components that commute with both $\hat{I}_z + \hat{S}_z$ and $\hat{I}_z - \hat{S}_z$.

It can be shown that the term $I_x S_x + I_y S_y$ in the dipolar Hamiltonian does not commute with the difference chemical shift $\hat{I}_z - \hat{S}_z$. Only the $I_z S_z$ term in the dipolar Hamiltonian remains after truncation:

$$\hat{H}_{IS}^{(0)} = -\hbar\omega_D \frac{1}{2} (3\cos^2\theta - 1) \cdot 2I_z S_z$$

Note that the exact calculation of the truncated Hamiltonian cannot be made based on the above argument, because while $I_x S_x$ and $I_y S_y$ do not commute with $\hat{I}_z - \hat{S}_z$, combinations of $I_x S_x$ and $I_y S_y$ can commute (see DQ and ZQ coherences later).

Homonuclear I-J dipolar coupling

For $\omega_I - \omega_S \sim \omega_D$ and $\omega_I - \omega_S < \omega_D$, we can neglect the chemical shift difference term and approximate the total CS Hamiltonian as

$$\hat{H}_0 \approx \frac{1}{2} \hbar (\omega_I + \omega_J) (\hat{I}_z + \hat{J}_z)$$

So only the sum chemical shift can truncate the dipolar Hamiltonian. The result of this truncation is:

$$\hat{H}_{IJ}^{(0)} = -\hbar \omega_D \frac{3 \cos^2 \theta - 1}{2} \cdot (3 I_z J_z - \hat{I} \cdot \hat{J})$$

1.4. Quadrupolar interaction

Spin-1/2 nuclei only have magnetic dipole moments. Higher multipole moments, both magnetic and electric, vanish, which can be proved using the Wigner-Eckert theorem.

Nuclei with spin quantum numbers $I \geq 1$ have an **electric** quadrupole moment Q , which, when subject to an **electric field gradient** V , produces an interaction that is **magnetic** in nature. So the size of the quadrupolar interaction depends both on the size of nuclear Q and the size of the electric field gradient created by the electrons at the site of the nucleus.

Metal nuclei tend to have large quadrupole moments but small EFGs due to the symmetric ionic environments, so their quadrupolar interaction is weak. In comparison, non-metal nuclei such as ^{14}N have small quadrupole moments Q but large EFGs due to the asymmetric covalent bonding (except for cases such as NH_4^+).

The EFG tensor is defined as:

$$V_{\alpha\beta} \equiv \frac{\partial E_\alpha}{\partial r_\beta} = \frac{\partial^2 \phi}{\partial r_\alpha \partial r_\beta} \Big|_{\text{at nucleus}}, \quad (\alpha, \beta = x, y, z), \text{ where } \phi \text{ is the electric potential.}$$

The EFG tensor is symmetric and traceless ($V_{xx} + V_{yy} + V_{zz} = 0$). We can define an asymmetry

parameter $\eta_Q \equiv \frac{V_{xx} - V_{yy}}{V_{zz}}$ just like the chemical shift asymmetry parameter. Then, the principal values of the EFG tensor can be re-written in terms of η_Q :

$$V_{xx} = -eq(1 - \eta_Q)/2, \quad V_{yy} = -eq(1 + \eta_Q)/2, \quad V_{zz} = e \cdot q \text{ (unit: } V/m^2)$$

The full quadrupolar interaction \hat{H}_Q is:

$$\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \hat{I} \cdot V \cdot \hat{I}$$

Similar to chemical shift, when the quadrupole interaction is much smaller than the Zeeman interaction, the latter truncates the quadrupolar interaction to first order. But the size of the quadrupolar interaction is often larger than chemical shielding, so second-order terms are often included.

$$\hat{H}_Q \approx \hat{H}_Q^{(1)} + \hat{H}_Q^{(2)} + \dots$$

(Note the conventional quadrupole interaction order starts with 1, while the other spin-1/2 interactions normally start with 0 for their truncated forms.)

The first-order quadrupolar interaction is:

$$\hat{H}_Q^{(1)} = \frac{1}{2} \frac{eQ}{2I(2I-1)\hbar} \cdot V_{zz}^{LF} (3\hat{I}_z^2 - I(I+1)\hat{1}) = \frac{\omega_Q^{(1)}}{6} (3\hat{I}_z^2 - I(I+1)\hat{1})$$

where $\omega_Q^{(1)} = \frac{3eQ \cdot V_{zz}^{LF}}{2I(2I-1)\hbar}$.

The 2nd order quadrupolar interaction is scaled down from the 1st order term by the Larmor frequency:

$$\omega_Q^{(2)} \sim \frac{\{\omega_Q^{(1)}\}^2}{\omega_0}$$

So the higher the magnetic field, the smaller the second-order quadrupolar coupling.

2. Spin Density Operators

We can use the vector model and classical mechanics to explain:

- Larmor precession
- effects of single-spin interactions such as chemical shifts on magnetization
- effects of rf pulses on single-spin magnetization

However, we cannot use the vector model to explain:

- the effect of two-spin interactions on the magnetization,
- evolution of coupled spin states

We need to use the density operator/matrix formalism for this purpose. Density operator ρ combines the quantum mechanics of a single spin with the statistical mechanics of an ensemble of spins.

2.1 Density operator defined

Most samples contain a statistical mixture of spins with different polarization states. The magnetization is the sum of the individual magnetic dipole moments. A single spin-1/2 in a superposition state of spin up and spin down can be expressed as:

$$|\psi\rangle = \begin{pmatrix} c_a \\ c_b \end{pmatrix} \quad \text{with basis states of } |\psi_a\rangle, |\psi_b\rangle$$

The expectation value of an operator is defined based on this pure state as:

$$\langle \hat{A} \rangle \equiv \langle \psi | A | \psi \rangle = \begin{pmatrix} c_a^* & c_b^* \end{pmatrix} \begin{pmatrix} A_{aa} & A_{ab} \\ A_{ba} & A_{bb} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = c_a^* c_a A_{aa} + c_b^* c_b A_{bb} + c_a^* c_b A_{ab} + c_b^* c_a A_{ba}$$

The products of coefficients such as $c_a^* c_a$ correspond to the elements of a density operator $\hat{\rho}$:

$$\hat{\rho} \equiv |\psi\rangle\langle\psi| = \begin{pmatrix} c_a \\ c_b \end{pmatrix} \begin{pmatrix} c_a^* & c_b^* \end{pmatrix} = \begin{pmatrix} c_a c_a^* & c_a c_b^* \\ c_b c_a^* & c_b c_b^* \end{pmatrix}$$

The density operator is Hermitian, i.e. $\hat{\rho}^* = \hat{\rho}$. The expectation value of any operator can then be written as the trace of the product between the density operator and the observable:

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho} \hat{A}) = \text{Tr}(|\psi\rangle\langle\psi| \hat{A})$$

For ensembles of spins with states $|\psi\rangle_i$ with different coefficients $c_{a,i}$, $c_{b,i}$:

$$\hat{\rho} \equiv \overline{|\psi\rangle\langle\psi|} = \frac{1}{N} \sum_i |\psi\rangle_i \langle\psi|_i = \begin{pmatrix} \overline{c_a c_a^*} & \overline{c_a c_b^*} \\ \overline{c_b c_a^*} & \overline{c_b c_b^*} \end{pmatrix} = \begin{pmatrix} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{pmatrix}$$

Density operator is a very useful construct because a mixture of spin system cannot be easily described as state vectors (coefficients are all different).

The expectation value of a physical observable for a QM system that is a mixture can still be calculated using the same formal equation, but with the density operator defined with the ensemble average bar:

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho} \hat{A})$$

Once the spin density operator of the ensemble is known, one can predict the measurement result (expectation value) of any physical observable, independent of the individual spin states.

2.2 Populations and coherences

The diagonal elements of the density operator are **populations**, since $\rho_{aa} = \overline{c_a c_a^*}$ gives the ensemble-averaged probability of finding the system in state a .

Populations are real and positive, and for normalized spin states, $\rho_{aa} + \rho_{bb} = \overline{c_a c_a^*} + \overline{c_b c_b^*} = 1$, i.e. $\text{Tr}(\hat{\rho}) = 1$. The difference in the populations corresponds to the net z magnetization.

The off-diagonal elements of the density matrix are **coherences** between spin eigenstates. Coherences are complex, and the two elements are complex conjugate of each other:

$$\rho_{ab} = \rho_{ab}^*, \quad \text{i.e. } \overline{c_a c_b^*} = \left(\overline{c_b c_a^*}\right)^2$$

The presence of non-zero coherence terms means there is transverse magnetization; moreover, the polarization vectors of individual spins' transverse dipole moment cannot all point to the same direction.

2.3 Density operator at thermal equilibrium

At thermal equilibrium, the coherences are 0 and the populations obey the Boltzmann distribution. So the diagonal elements of the density matrix are:

$$\rho_{ii}^{eq} = \frac{e^{-\hbar\omega_i/kT}}{\sum_i e^{-\hbar\omega_i/kT}}.$$

For most NMR experiments, $\hbar\omega_i/kT \ll 1$. Therefore, $e^{-\hbar\omega_i/kT} \approx 1 - \hbar\omega_i/kT$

In operator terms:

$$\hat{\rho}^{eq} = \frac{e^{-\hat{H}/kT}}{\text{Tr}\left(e^{-\hat{H}/kT}\right)}$$

The exponential operator can be Taylor-expanded as $e^{-\hat{H}/kT} = 1 - \frac{\hat{H}}{kT} + \frac{1}{2!} \left(\frac{\hat{H}}{kT}\right)^2 + \dots$

For typical magnetic field strengths of several Tesla, $\hat{H} = \hbar\omega_0 \hat{I}_z$ is very small compared to thermal energy:

$$\frac{\hbar\omega_0}{kT} \sim \frac{400 \cdot 10^6 \cdot 6.626 \cdot 10^{-34}}{1.38 \cdot 10^{-23} \cdot 300} \sim 10^{-5} \ll 1.$$

As long as $T \gg 1\text{K}$, the above equation holds true, since the Boltzmann factor is only 10^{-5} to 10^{-3} . So we can safely consider only the first two terms of the Taylor series:

$$\hat{\rho}^{eq} \approx \frac{1}{\text{Tr}\left(e^{-\hat{H}/kT}\right)} \left(1 + \frac{\hbar\omega_0}{kT} \hat{I}_z\right)$$

The trace of the density operator is $\text{Tr}\left(e^{-\hat{H}/kT}\right) \approx 1 + 1 = 2$. Since $\hat{I}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, the density operator can be expressed as the following matrix:

$$\hat{\rho}^{eq} \approx \begin{pmatrix} \frac{1}{2} + \frac{1}{4} \frac{\hbar\omega_0}{kT} & 0 \\ 0 & \frac{1}{2} - \frac{1}{4} \frac{\hbar\omega_0}{kT} \end{pmatrix}$$

The unit operator is unaffected by any Hamiltonian, so we can focus on the reduced density operator:

$$\hat{\rho}_{reduced}^{eq} = \frac{1}{Z} \left(\frac{\hbar\omega_0}{kT} \hat{I}_z \right)$$

2.4 NMR observables

In NMR, the only observables are single-quantum magnetization components:

$$\gamma \hbar \langle \hat{I} \rangle \approx \begin{pmatrix} \langle I_x \rangle \\ \langle I_y \rangle \\ \langle I_z \rangle \end{pmatrix} = \begin{pmatrix} Tr(\rho I_x) \\ Tr(\rho I_y) \\ Tr(\rho I_z) \end{pmatrix}$$

This means that for there to be detectable magnetization, the density operator itself must contain terms such as $\hat{\rho} = c\hat{I}_x, c\hat{I}_y, c\hat{I}_z$, so that the expectation values do not vanish. If $\hat{\rho} = c\hat{I}_x$, then

$$\langle I_x \rangle = Tr(\rho I_x) = c Tr \left[\frac{1}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right] = \frac{c}{4} Tr \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{c}{2}$$

$$\text{while } \langle I_y \rangle = Tr(\rho I_y) = c Tr \left[\frac{1}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \right] = \frac{c}{4} Tr \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} = 0 \text{ and } \langle I_z \rangle = Tr(\rho I_z) = 0$$

In other words,

$$\hat{\rho} = c\hat{I}_x \text{ means that only } \langle I_x \rangle \neq 0,$$

$$\hat{\rho} = c\hat{I}_y \text{ means that only } \langle I_y \rangle \neq 0$$

$$\text{and } \hat{\rho} = c\hat{I}_z \text{ means that only } \langle I_z \rangle \neq 0$$

We can thus interpret $\hat{\rho} = c\hat{I}_i$ as detectable magnetization along the i axis, without explicitly calculating expectation values every time. All NMR experiments produce final density operators of this form, whose associated frequencies encode structural and dynamical information.

2.5 Time evolution of the density operator under a Hamiltonian

The Schrodinger equation describes how a state evolves under an H:

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

Multiplying the equivalent bra equation to both sides, we obtain the corresponding equation of motion for the density operator:

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

Note: Proof of von Neumann equation from the Schrödinger equation:

$$\begin{aligned} \frac{d\hat{\rho}}{dt} &= \frac{d|\psi\rangle\langle\psi|}{dt} = \frac{d|\psi\rangle}{dt}\langle\psi| + |\psi\rangle\frac{d\langle\psi|}{dt} = -\frac{i}{\hbar} H|\psi\rangle\langle\psi| + |\psi\rangle\frac{i}{\hbar}\langle\psi|H \\ &= -\frac{i}{\hbar}(H|\psi\rangle\langle\psi| - |\psi\rangle\langle\psi|H) = -\frac{i}{\hbar}[H, \hat{\rho}] \end{aligned}$$

This **von Neumann** equation expresses time dependence in terms of an operator instead of states, and is a manifestation of the Heisenberg picture of quantum mechanics.

If the Hamiltonian and the density operator commute, i.e. $[\hat{H}, \hat{\rho}(t)] = 0$, then ρ does not change with time. For example, when the magnetization is along the z direction, $\rho = I_z$, then it does not evolve under the chemical shift interaction nor the dipolar interaction.

For time-independent Hamiltonians, the formal solution of the von Neumann equation is:

$$\rho(t) = e^{-iHt} \rho(0) e^{iHt}$$

where $U(t) \equiv e^{-iHt}$ is called the **propagator**, as it propagates ρ in time. i.e.

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

As before, the exponential operator can be Taylor-expanded as:

$$e^{\hat{A}} = 1 + \frac{\hat{A}}{1!} + \frac{\hat{A} \cdot \hat{A}}{2!} + \dots$$

A more useful form of the solution is to Taylor-expand the formal solution to obtain a series called the **Baker-Hausdorff series**, which can be simplified considerably under certain conditions:

$$\begin{aligned}
\rho(t) &= \left(1 - iHt + \frac{(iHt)^2}{2!} \dots\right) \rho(0) \left(1 + iHt + \frac{(iHt)^2}{2!} \dots\right) \\
&= \rho(0) + [-iHt, \rho(0)] + \frac{1}{2!} [-iHt, [-iHt, \rho(0)]] + \frac{1}{3!} [-iHt, [-iHt, [-iHt, \rho(0)]]] + \dots \\
&= \rho(0) - \frac{it}{1!} \underbrace{[H, \rho(0)]}_{r_1} + \frac{(it)^2}{2!} \underbrace{[H, [H, \rho(0)]]}_{r_2} - \frac{(it)^3}{3!} [H, r_2] + \dots
\end{aligned}$$

If $r_2 = [H, [H, \rho(0)]] = \rho(0) \cdot \omega^2$, then the series converges as $r_3 = r_1 \cdot \omega^2, r_5 = r_3 \cdot \omega^2, r_4 = r_2 \cdot \omega^2$

Under this condition,

$$\rho(t) = \rho(0) \left(1 + \frac{(i\omega t)^2}{2!} + \frac{(i\omega t)^4}{4!} + \dots\right) + \frac{i[H, \rho(0)]}{\omega} \left(\frac{(i\omega t)^1}{1!} + \frac{(i\omega t)^3}{3!} + \dots\right)$$

$$\rho(t) = \rho(0) \cos \omega t - \frac{i[H, \rho(0)]}{\omega} \sin \omega t$$

Where ω is the proportionality constant in $r_2 = \rho(0) \cdot \omega^2$.

Note that the coefficients in front of the sine function are such that the imaginary i will disappear, because the commutator always contains an i , and the denominator will also disappear because the commutator contains the same frequency.

3. Application of the von Neumann equation to simple NMR experiments

3.1 Larmor precession and chemical shift evolution:

Let $\rho(0) = I_x$, which can be created by a 90° pulse along y. Consider the Hamiltonian $H = \omega_0 I_z$. The formal solution of $\rho(t)$ is $\rho(t) = e^{-iHt} \cdot I_x \cdot e^{iHt} = e^{-i\omega_0 I_z t} \cdot I_x \cdot e^{i\omega_0 I_z t}$. More usefully,

$$\begin{aligned}
[H, \rho(0)] &= [\omega_0 I_z, I_x] = i\omega_0 I_y \\
[H, [H, \rho(0)]] &= [\omega_0 I_z, i\omega_0 I_y] = \omega_0^2 I_x = \omega_0^2 \rho(0)
\end{aligned}$$

So the $r_2 = \rho(0) \cdot \omega^2$ condition is met. Therefore,

$$\rho(t) = I_x \cos \omega_0 t - \frac{i \cdot i\omega_0 I_y}{\omega_0} \sin \omega_0 t = I_x \cos \omega_0 t + I_y \sin \omega_0 t$$

This equation describes precession of the x magnetization in the transverse plane around the z axis.

3.2 Heteronuclear dipolar or J coupling

Let S be the observed spin and I the coupled spin. Consider an isolated I-S spin system.

Initially, we apply a 90° pulse on the S channel: $\rho(0) = aS_x + bI_z$, where a and b differ due to the Boltzmann factor for spins with different gyromagnetic ratios

The truncated heteronuclear dipolar Hamiltonian is $H_{IS} = 2\omega_d I_z S_z$

Since I_z commutes with $I_z S_z$, I spin does not change with time.

$$[H, \rho(0)] = [2\omega_d I_z S_z, aS_x] = 2a\omega_d I_z [S_z, S_x] = 2ai\omega_d I_z S_y$$

$$[H, [H, \rho(0)]] = [2\omega_d I_z S_z, 2ai\omega_d I_z S_y] = 4ia\omega_d^2 I_z^2 [S_z, S_y] = 4i\omega_d^2 \frac{1}{4} (-i) S_x = \omega_d^2 (aS_x)$$

So the cyclic condition is satisfied with a proportionality constant of ω_d , and the Baker-Hausdorff series converges to

$$\begin{aligned} \rho(t) &= \rho(0) \cos \omega_d t - \frac{i[H, \rho(0)]}{\omega_d} \sin \omega_d t \\ &= bI_z + aS_x \cos \omega_d t - \frac{i2ai\omega_d I_z S_y}{\omega_d} \sin \omega_d t = bI_z + aS_x \cos \omega_d t + 2aI_z S_y \sin \omega_d t \end{aligned}$$

So the S-spin signal is modulated by $\cos \omega_d t$, and should show two peaks symmetric with respect to the 0 frequency.

3.3 Quadrature detection of NMR signals

In NMR, quadrature detection means detecting $\langle I^+ \rangle = \langle I_x + iI_y \rangle$, where the raising operator in matrix

$$\text{form is } I^+ = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \frac{i}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

Since $\langle A \rangle = \text{Tr}(\rho A)$, $\langle I^+ \rangle = \text{Tr}(\rho I^+)$.

Take $\rho(t) = I_x \cos \omega_0 t + I_y \sin \omega_0 t$. Then the density operator at time t is:

$$\rho(t) = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cos \omega_0 t + \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \sin \omega_0 t = \frac{1}{2} \begin{pmatrix} 0 & e^{-i\omega_0 t} \\ e^{i\omega_0 t} & 0 \end{pmatrix}$$

The expectation value of the quadrature detected spin operator is:

$$\langle I^+ \rangle = \text{Tr} \left[\frac{1}{2} \begin{pmatrix} 0 & e^{-i\omega_0 t} \\ e^{i\omega_0 t} & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \right] = \frac{1}{2} \text{Tr} \begin{pmatrix} 0 & 0 \\ 0 & e^{i\omega_0 t} \end{pmatrix} = \frac{1}{2} e^{i\omega_0 t}$$

So the detected signal is $f(t) = \frac{1}{2}(\cos \omega_0 t + i \sin \omega_0 t)$ for $\rho(t) = I_x \cos \omega_0 t + I_y \sin \omega_0 t$. Detection is equivalent to picking out the spatial part of the density operator. The factor of $\frac{1}{2}$ comes from the spin-1/2 of the operator.

3.4 Hahn Echo

I spin: $90^\circ_x - t - 180^\circ_y - t$ - detect

$$\begin{aligned} \rho(0) \propto I_z &\xrightarrow{90^\circ I_x} I_y \xrightarrow{H=\omega_I I_z t} I_y \cos \omega_I t - I_x \sin \omega_I t \xrightarrow{180^\circ I_y} I_y \cos \omega_I t + I_x \sin \omega_I t \\ &\xrightarrow{H=\omega_I I_z t} I_y \cos^2 \omega_I t - I_x \cos \omega_I t \sin \omega_I t + I_x \sin \omega_I t \cos \omega_I t + I_y \sin^2 \omega_I t \\ &= I_y \end{aligned}$$

If we change the 180° pulse phase to x: $90^\circ_x - t - 180^\circ_x - t$ - detect

$$\begin{aligned} I_y \cos \omega_I t - I_x \sin \omega_I t &\xrightarrow{180^\circ I_x} -I_y \cos \omega_I t - I_x \sin \omega_I t \\ &\xrightarrow{H=\omega_I I_z t} -I_y \cos^2 \omega_I t + I_x \cos \omega_I t \sin \omega_I t - I_x \sin \omega_I t \cos \omega_I t - I_y \sin^2 \omega_I t = -I_y \end{aligned}$$

The direction of the M is inverted. This is the basis of the exorcycle phase cycling that we discussed before.

----- Matrix algebra review -----

Commuting operators

In general, operator products depend on the direction of multiplication. This property differs from products of scalar quantities.

The commutator between two operators is defined as: $[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$

Two operators \hat{A} and \hat{B} commute if and only if $[\hat{A}, \hat{B}] = 0$, i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$.

Two operators do not commute if $[\hat{A}, \hat{B}] \neq 0$.

Pauli matrices

For spin-1/2, three Pauli matrices, corresponding to the three orthogonal directions of the spin operator, can be defined:

$$\hat{I}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \hat{I}_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \hat{I}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \hat{I}_x^2 = \hat{I}_y^2 = \hat{I}_z^2 = \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{4} \hat{1}$$

$$[\hat{I}_x, \hat{I}_y] = i\hat{I}_z, [\hat{I}_y, \hat{I}_z] = i\hat{I}_x, [\hat{I}_z, \hat{I}_x] = i\hat{I}_y$$

Two-spin operators

Products of two spin operators are tensor products that increase the dimensionality of the matrices from 2 to 4 for two spin-1/2 systems.

$$\begin{aligned} \text{e.g. } \hat{I}_x \hat{I}_y &= \frac{1}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} \\ \hat{I}_x \hat{I}_x &= \frac{1}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \\ \hat{I}_z \hat{I}_z &= \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \end{aligned}$$

These matrices allow us to calculate the commutator of two-spin product operators.

$$\text{e.g. } [\hat{I}_x \hat{S}_x, \hat{I}_z \hat{S}_z] = ?$$

$$\begin{aligned} \hat{I}_x \hat{I}_x \hat{S}_z \hat{S}_z - \hat{S}_z \hat{S}_z \hat{I}_x \hat{I}_x &\propto \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} - \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} = 0 \end{aligned}$$

$$\text{So } [\hat{I}_x \hat{S}_x, \hat{I}_z \hat{S}_z] = 0$$

What about the commutator between $\hat{I}_x \hat{S}_x$ and the sum spin operator, $\hat{I}_z + \hat{S}_z$? The latter is important because the combined chemical shift and Zeeman interaction of two spins is $\hat{I}_z + \hat{S}_z$.

$$\begin{aligned}\hat{I}_z + \hat{S}_z &= \hat{I}_z \otimes 1 + 1 \otimes \hat{S}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}\end{aligned}$$

$$\begin{aligned}\text{So, } [\hat{I}_x \hat{S}_x, \hat{I}_z + \hat{S}_z] &= \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} - \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \neq 0\end{aligned}$$

We can summarize the following two-spin operators:

$$\hat{I}_x \hat{S}_x = \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad \hat{I}_y \hat{S}_y = \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}, \quad \hat{I}_z \hat{S}_z = \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Other notable matrices are:

$$\hat{I}_z + \hat{S}_z = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad \hat{I} \cdot \hat{S} = \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

In general, a single product operator of two spins with double-transverse components does not commute with $\hat{I}_z + \hat{S}_z$. However, combinations of two product operators can commute. The commutation of two-spin product operators can be cast in the fictitious spin-1/2 framework to facilitate the calculation of the time evolution of coherences under double-quantum and zero-quantum Hamiltonians.

Lectures #2: Average Hamiltonian Theory

Average Hamiltonian theory (AHT), developed by Waugh and Haeberlen in 1968, is a mathematical formalism for analyzing how pulse sequences affect internal spin interactions. AHT is particularly useful in the derivation and analysis of pulse sequences that consist of a block of rf pulses repeated many times. This is the situation that arises in many homonuclear decoupling and dipolar recoupling experiments.

AHT depends on changing the picture in which we view the evolution of the spin system from the usual rotating frame of the Zeeman interaction to a new frame of reference in which the rf pulses no longer appear directly. Instead, the rf pulses cause additional time dependences in the local fields (H_D , H_{CSA} , and H_{CS}). This new frame is called the interaction representation of the rf Hamiltonian.

1. Interaction frame

1.1 Interaction frame of the Zeeman interaction: the rotating frame

We have already discussed an interaction frame extensively before: the rotating frame is the interaction frame of the Zeeman interaction.

Larmor precession in the laboratory frame is mathematically represented as:

$$\rho(t) = e^{-iH_0 t} \rho(0) e^{+iH_0 t} = e^{-i\omega_0 I_z t} \rho(0) e^{i\omega_0 I_z t} \quad (1)$$

The transition to a frame rotating at $\omega_R = \omega_0$, where the magnetization appears static, is equivalent to a sign-reversed exponential operator rotation:

$$\rho_R(t) = e^{i\omega_R I_z t} \cdot \rho(t) \cdot e^{-i\omega_R I_z t} \quad (2)$$

Eq. 2 differs from Eq. 1 in that the central operator is $\rho(t)$ rather than $\rho(0)$, and the sign of the exponential operator is opposite.

Eq. 2 describes the density operator in the interaction frame of the Zeeman Hamiltonian.

Combining Eq. 1 and 2, we find the time evolution of the rotating-frame density operator as:

$$\rho_R(t) = e^{i(\omega_R - \omega_0) I_z t} \cdot \rho(0) \cdot e^{-i(\omega_R - \omega_0) I_z t} \quad (3)$$

This shows that the offset $\omega_0 - \omega_R$ governs the evolution of M in the rotating frame.

1.2 General definition of the interaction representation and truncation

In general, for a Hamiltonian consisting of a large H_0 and a small H_1 , $H = H_0 + H_1$, H_1 can be transformed into the interaction frame of H_0 according to

$$\tilde{H}_1(t) \equiv e^{iH_0 t} H_1 e^{-iH_0 t} \quad (4)$$

The density operator is transformed into the interaction frame of H_0 as:

$$\tilde{\rho}(t) \equiv e^{iH_0 t} \rho(t) e^{-iH_0 t} \quad (5)$$

In this H_0 interaction frame, the equation of motion is similar to the von Neumann eqn:

$$\frac{d\tilde{\rho}}{dt} = -i[\tilde{H}_1, \tilde{\rho}] \quad (6)$$

The components of H_1 that do not commute with H_0 appear as time-dependent, $\tilde{H}_1(t)$. If $H_0 \gg H_1$, then the time oscillations due to H_0 are much faster than the time dependence of H_1 itself. Then, the effects of these non-commuting terms are averaged to 0. The time-averaged H_1 in the interaction representation is therefore:

$$\overline{\tilde{H}_1}^{(0)} = \overline{e^{iH_0 t} H_1 e^{-iH_0 t}}, \quad (7)$$

which is again time independent.

Eq. (7) is the definition of **truncation** of H_1 by H_0 . The time averaging retains only parts of H_1 that commute with H_0 . (We will see below that truncation is basically first-order average Hamiltonian theory).

In the interaction representation, the density operator evolves under $\overline{\tilde{H}_1}^{(0)}$ according to:

$$\tilde{\rho}(t) = e^{-i\overline{\tilde{H}_1}^{(0)} t} \tilde{\rho}(0) e^{i\overline{\tilde{H}_1}^{(0)} t}, \quad (8)$$

Eventually, we want to know the density operator in the laboratory frame. Since

$$\tilde{\rho}(t) = e^{iH_0 t} \rho(t) e^{-iH_0 t}, \quad \rho(t) = e^{-iH_0 t} \tilde{\rho}(t) e^{iH_0 t}, \quad (9)$$

we find:

$$\rho(t) = e^{-iH_0 t} \left[e^{-i\overline{\tilde{H}_1}^{(0)} t} \tilde{\rho}(0) e^{i\overline{\tilde{H}_1}^{(0)} t} \right] e^{iH_0 t} = e^{-i(H_0 + \overline{\tilde{H}_1}^{(0)}) t} \rho(0) e^{i(H_0 + \overline{\tilde{H}_1}^{(0)}) t} \quad (10)$$

Back in the laboratory frame, we know that the normal solution to the von Neumann equation is:

$$\rho(t) = e^{-i(H_0 + H_1) t} \rho(0) e^{i(H_0 + H_1) t}, \quad (11)$$

Comparing Eq. 10 and 11, we see that the transformation to the interaction frame amounts to replacing H_1 by its first-order time average:

$$e^{-i(H_0+H_1)t} \approx e^{-i(H_0+\overline{H}_1^0)t} \quad (12)$$

1.3 Interaction frame of the rf Hamiltonian H_{rf}

The interaction frame is a very useful tool for calculating the effective local fields under rf pulses. When these rf pulses are stronger than the local spin Hamiltonians, $\omega_1 \gg \omega_{I,S,H}$, we can transform the local spin Hamiltonians into the interaction frame of the rf pulses.

For a Hamiltonian consisting of a $H_{rf} = \omega_1 I_\alpha = -\gamma B_1 I_\alpha$ which is larger than H_1 , $H = H_{rf} + H_1$, H_1 is transformed into the interaction frame of H_{rf} according to

$$\widetilde{H}_1(t) = e^{iH_{rf}t} H_1 e^{-iH_{rf}t} \quad (13)$$

The effect of the pulses is to rotate the nuclear spin interaction, similar to the von Neumann equation for density operators, **except for a sign change of the exponent**.

We can designate the propagator of the rf pulse as $P \equiv e^{-iH_{rf}t}$. In the literature, this is more commonly written as the evolution operator U_{rf} . Then eq. 13 can be rewritten as

$$\widetilde{H}_1(t) = P^{-1} \cdot H_1 \cdot P \quad \text{or} \quad = U_{rf}^{-1} \cdot H_1 \cdot U_{rf} \quad (14)$$

We are interested in the average H_1 in the interaction representation of the rf pulses (cf eq 7):

$$\overline{\widetilde{H}_1}^{(0)} = \frac{1}{t_c} \int_0^{t_c} e^{iH_{rf}t} H_1 e^{-iH_{rf}t} dt, \quad (15)$$

This averaging requires that the rf pulse sequence is periodic over a cycle time t_c .

For multi-pulse sequences, we can determine the interaction-frame spin Hamiltonians visually by toggling the frame of the internal Hamiltonians (see KSR/Spiess Chapter 3):

- 1) Flip the interaction frame with the pulses in the rotating frame (left hand rule) around the axis of the pulse,
- 2) the axis of the interaction representation coordinate system that is parallel to the z-axis of the rotating frame is the direction of \widetilde{H}_1 .
- 3) Sum all the \widetilde{H}_1 directions for all periods to obtain the average Hamiltonian.

The density operator is similarly transformed into the interaction frame of H_{rf} :

$$\widetilde{\rho}(t) = e^{iH_{rf}t} \rho(t) e^{-iH_{rf}t} = U_{rf}^{-1} \cdot \rho(t) \cdot U_{rf} \quad (16)$$

In this interaction frame, the equation of motion is

$$\frac{d\tilde{\rho}}{dt} = -i[\widetilde{H}_1, \tilde{\rho}] \quad (17)$$

which allows us to calculate $\rho(t)$ in the interaction frame just like in the lab frame. But similar to our truncation description, one cannot “go into” the interaction frame without knowing how to “come back” to the lab frame. We must write down the entire density operator equality as:

$$\rho(t) = U \cdot \rho(0) \cdot U^{-1} = T e^{-i \int_0^t dt' (H_1 + H_{rf})} \cdot \rho(0) \cdot T e^{i \int_0^t dt' (H_1 + H_{rf})} \quad (18a)$$

$$= \underbrace{T e^{-i H_{rf} t}}_{U_{rf}(t)} \underbrace{T e^{-i \int_0^t dt' \widetilde{H}_1}}_{\widetilde{U}(t)} \cdot \rho(0) \cdot T e^{i \int_0^t dt' \widetilde{H}_1} \underbrace{T e^{i H_{rf} t}}_{U_{rf}^{-1}(t)} = U_{rf} \widetilde{U}_1 \cdot \rho(0) \cdot \widetilde{U}_1^{-1} U_{rf}^{-1} \quad (18b)$$

Here T is the Dyson time-ordering operator, and

$$\widetilde{H}_1 = U_{rf}^{-1} H_1 U_{rf} = e^{i H_{rf} t} H_1 e^{-i H_{rf} t} \quad (19)$$

Using the equality $e^A e^B e^C = \exp(e^A \cdot B \cdot e^C)$, Eq. 18b can be proved as:

$$\begin{aligned} \rho(t) &= U_1 U_{rf} \cdot \rho(0) \cdot U_{rf}^{-1} U^{-1} = U_{rf} \underbrace{U_{rf}^{-1} U_1 U_{rf}} \cdot \rho(0) \cdot \underbrace{U_{rf}^{-1} U^{-1} U_{rf}} U_{rf}^{-1} \\ &= U_{rf} e^{-i \int_0^t dt' \widetilde{H}_1} \cdot \rho(0) \cdot e^{i \int_0^t dt' \widetilde{H}_1} U_{rf}^{-1} \end{aligned} \quad (20)$$

For cyclic sequences, $U_{rf}(t_c) \equiv T e^{-i H_{rf} t_c} = 1$. Therefore, for calculating the average Hamiltonian over the cycle time, the rf term can be removed from Eq. 18.

We replace the time integral of \widetilde{H}_1 by an effective Hamiltonian $\widetilde{\widetilde{H}}_1$

$$\begin{aligned} \rho(t) &= U_{rf} T e^{-i \int_0^t dt' \widetilde{H}_1} \cdot \rho(0) \cdot T e^{i \int_0^t dt' \widetilde{H}_1} U_{rf}^{-1} \\ &= U_{rf} e^{-i \widetilde{\widetilde{H}}_1 t_c} \cdot \rho(0) \cdot e^{i \widetilde{\widetilde{H}}_1 t_c} U_{rf}^{-1} \end{aligned} \quad (21)$$

where $\widetilde{\widetilde{H}}_1$ is equal to an infinite series called the **Magnus expansion**:

$$\begin{aligned} \widetilde{\widetilde{H}}_1 &= \widetilde{\widetilde{H}}_1^{(0)} + \widetilde{\widetilde{H}}_1^{(1)} + \widetilde{\widetilde{H}}_1^{(2)} + \dots \\ &= \frac{1}{t_c} \int_0^{t_c} dt_1 \widetilde{H}_1 \quad \text{the 1st-order term is the simple average in Eq. 7 and Eq. 15} \\ &\quad + \frac{1}{2it_c} \int_0^{t_c} dt_1 \int_0^{t_1} [\widetilde{H}_1(t_1), \widetilde{H}_1(t_2)] dt_2 \\ &\quad - \frac{1}{6t_c} \int_0^{t_c} dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} \{ [\widetilde{H}_1(t_1), [\widetilde{H}_1(t_2), \widetilde{H}_1(t_3)]] + [\widetilde{H}_1(t_3), [\widetilde{H}_1(t_2), \widetilde{H}_1(t_1)]] \} dt_3 \end{aligned} \quad (22)$$

The higher-order terms in the effective Hamiltonian are relevant when the time tau between pulses are not negligible compared to the inverse of the interaction strength. These higher-order terms are the reasons for the different performances of various multiple-pulse decoupling and dipolar recoupling sequences.

The sign of rotation in the AHT and interaction representation

The exponential operators in the time evolution of the density operator

$$\rho(t) = e^{-iHt} \rho(0) e^{iHt} = U \rho(0) U^{-1}$$

have the opposite sign from the sign in the interaction transformation

$$\widetilde{H}_1 = e^{iH_{rf}t} H_1 e^{-iH_{rf}t} = U_{rf}^{-1} H_1 U_{rf}.$$

This means that the rotation happens with the opposite sign from the ρ evolution, and the order of the pulses in a sequence is multiplied onto H_1 in a reversed fashion.

Summary of the AHT

When

- 1) the rf pulse sequence and the internal spin interactions are periodic over a cycle time t_c , and
- 2) the net rotation produced by the rf block is zero, $U_{rf}(t_c) \equiv T e^{-iH_{rf}t_c} = 1$,

then we can apply the AHT to convert the problem of finding the propagator $U(t)$ for the entire sequence to the problem of finding the interaction-frame propagator $\widetilde{U}(t_c) = e^{-i\widetilde{H}_1 t_c}$, where the rf pulses have been transformed away.

Once we can calculate the effective Hamiltonian \widetilde{H}_1 , which is usually done at the first-order term, $\widetilde{H}_1^{(0)}$, then we can calculate the time evolution of the density operator.

2. Using AHT to analyze simple NMR experiments

2.1 Chemical shift interaction under a spin lock pulse along x

$$H_{cs} = \omega_{cs} I_z, \quad H_{rf} = \omega_1 I_x$$

Transform into the interaction frame of the rf pulse:

$$\widetilde{H}_{cs}(t) = e^{i\omega_1 I_x t} \omega_{cs} I_z e^{-i\omega_1 I_x t} = \omega_{cs} (I_z \cos \omega_1 t + I_y \sin \omega_1 t).$$

So the average CS interaction is:

$$\overline{H_{CS}} = \frac{1}{t_p} \omega_{CS} \int_0^{t_p} (I_z \cos \omega_1 t + I_y \sin \omega_1 t) dt = \frac{\omega_{CS}}{\omega_1 t_p} (I_z \sin \omega_1 t - I_y \cos \omega_1 t) \Big|_0^{t_p}$$

$$\text{When } t_p = \frac{2\pi}{\omega_1}, \quad \overline{H_{CS}} = 0.$$

$$\text{When } t_p \rightarrow \infty, \quad \overline{H_{CS}} \rightarrow 0.$$

You can show the same result by sketching the direction of the interaction-frame Hamiltonian as toggled by the rf pulses.

2.2 Heteronuclear decoupling by continuous irradiation

The heteronuclear dipolar coupling is $H_{IS} = \omega_d I_z S_z$. We consider the effect of continuous rf pulse $H_{rf} = \omega_1 I_x$ on the I channel on the S-spin signals. Since the continuous I-pulse affects only the I-spin operator, we obtain:

$$\overline{H_{IS}} = \frac{1}{t_p} \omega_d \int_0^{t_p} (I_z \cos \omega_1 t + I_y \sin \omega_1 t) S_z dt = \frac{\omega_d}{\omega_1 t_p} S_z (I_z \sin \omega_1 t - I_y \cos \omega_1 t) \Big|_0^{t_p} = 0.$$

Thus heteronuclear coupling is removed by continuous rotation of the I-spin operator by the pulses.

2.3 Homonuclear dipolar interaction under spin lock

Here we apply a continuous irradiation along the same direction as the magnetization after an initial 90° pulse. For example, 90° -y – spin lock x.

The homonuclear interaction is $H_{II} = \omega_d (3I_z J_z - I \cdot J)$. We can use the notation H_{zz} , to indicate that the spin operator direction is along z.

$$\begin{aligned} \overline{H_{II}} &= \frac{\omega_d}{t_p} \int_0^{t_p} \left[3(I_z \cos \omega_1 t + I_y \sin \omega_1 t)(J_z \cos \omega_1 t + J_y \sin \omega_1 t) - I \cdot J \right] dt \\ &= \frac{\omega_d}{t_p} \int_0^{t_p} \left[3(I_z J_z \cos^2 \omega_1 t + I_y J_y \sin^2 \omega_1 t + (I_z J_y + I_y J_z) \cos \omega_1 t \sin \omega_1 t) - I \cdot J \right] dt \\ &= \frac{\omega_d}{t_p} \int_0^{t_p} \left[\frac{3}{2}(I_z J_z + I_y J_y) - I \cdot J \right] dt = \omega_d \left[\frac{3}{2}(I \cdot J - I_x J_x) - I \cdot J \right] \\ &= -\omega_d \frac{1}{2} (3I_x J_x - I \cdot J) = -\frac{1}{2} H_{xx} \end{aligned}$$

So the average homonuclear dipolar Hamiltonian is half the size of the lab-frame homonuclear coupling and opposite in sign.

Magic zero: $(3I_x J_x - I \cdot J) + (3I_y J_y - I \cdot J) + (3I_z J_z - I \cdot J) = 0$

Since after the 90° pulse the magnetization is along x, $\rho(0) = I_x$, the magnetization does not evolve under the effective homonuclear coupling H_{xx} (they commute).

2.4 Cross polarization: heteronuclear dipolar interaction under double spin lock

The condition of CP is that $\omega_{1,I} = \omega_{1,S}$ (Hartman-Hahn matching).

$$\begin{aligned} \overline{\tilde{H}_{IS}} &= \frac{2\omega_d}{t_p} \int_0^{t_p} \left[(I_z \cos \omega_{1,I} t + I_y \sin \omega_{1,I} t) (S_z \cos \omega_{1,S} t + S_y \sin \omega_{1,S} t) \right] dt \\ &\stackrel{\omega_{1,I} = \omega_{1,S}}{\cong} \frac{2\omega_d}{t_p} \int_0^{t_p} \left[(I_z S_z \cos^2 \omega_1 t + I_y S_y \sin^2 \omega_1 t + (I_z S_y + I_y S_z) \cos \omega_1 t \sin \omega_1 t) \right] dt \\ &= \frac{2\omega_d}{t_p} \frac{1}{2} (I_z S_z + I_y S_y) t_p = \omega_d (I_z S_z + I_y S_y) \end{aligned}$$

When the Hartman-Hahn matching condition is satisfied, the interaction frames of the I and S spins precess synchronously, giving a non-zero heteronuclear dipolar Hamiltonian.

The important thing now is to analyze the density operator evolution.

$\rho(0) = I_x$. We want to write this in a more meaningful way to facilitate calculation.

$$\rho(0) = \frac{1}{2}(I_x + S_x) + \frac{1}{2}(I_x - S_x) = \rho^\Sigma(0) + \rho^\Delta(0).$$

$$\left[\overline{\tilde{H}_{IS}}, \rho(0) \right] = \omega_d \left[I_z S_z + I_y S_y, I_x \right] = \omega_d i (I_y S_z - I_z S_y)$$

Double commutator:

$$\begin{aligned} \left[\overline{\tilde{H}_{IS}}, \left[\overline{\tilde{H}_{IS}}, \rho(0) \right] \right] &= \omega_d^2 i \left[I_z S_z + I_y S_y, I_y S_z - I_z S_y \right] = \omega_d^2 i \left(-i I_x \frac{1}{4} + \frac{1}{4} i S_x + \frac{1}{4} i S_x - i I_x \frac{1}{4} \right) \\ &= \frac{1}{2} \omega_d^2 (I_x - S_x) \propto \rho^\Delta(0) \end{aligned}$$

So the difference part of the initial density operator will evolve under the average Hamiltonian,

$$\rho^\Delta(t) = \rho^\Delta(0) \cos \omega_d t + (I_y S_z - I_z S_y) \sin \omega_d t.$$

Combining with the sum part, we obtain:

$$\begin{aligned}\rho(t) &= \frac{1}{2}(I_x + S_x) + \frac{1}{2}(I_x - S_x)\cos\omega_d t + (I_y S_z - I_z S_y)\cos\omega_d t \\ &= \frac{1}{2}I_x(1 + \cos\omega_d t) + \frac{1}{2}S_x(1 - \cos\omega_d t) + \underbrace{(I_y S_z - I_z S_y)\cos\omega_d t}_{\text{invisible}}.\end{aligned}$$

How does CP enhance sensitivity?

Because the initial density operator has the Boltzmann factor of the I spin, $\rho(0) = \frac{\gamma_I B_0}{kT} I_x$. This factor

is now transferred to the S spin, $\rho(t) = \dots + \frac{\gamma_I B_0}{kT} S_x(1 - \cos\omega_d t) \dots$

It turns out that difference operators such as $I_x - S_x$ are in the zero-quantum space, while sum operators such as $(I_x + S_x)$ live in the double-quantum space. The CP average Hamiltonian, $I_z S_z + I_y S_y$, also belongs to the zero-quantum space, hence the evolution of the difference density operator under the CP Hamiltonian. In general, spin operators in the double-quantum space always commute with spin operators in the zero-quantum space, which means there is no evolution.

Bottom line: CP is a zero-quantum (ZQ) process.

The ZQ and DQ operators are defined as linear superpositions of the ladder operators. Zero quantum means one spin up and the other spin down, or double-quantum means both spins up or down together. The commutation properties of these two-spin operators can be more easily remembered, by defining fictitious spin-1/2 operators as the following:

4.5 Fictitious spin-1/2 operators

Zero-quantum space:

$$I_x^{(23)} \equiv \frac{1}{2}(I^+ S^- + I^- S^+) = I_x S_x + I_y S_y, \quad I_y^{(23)} \equiv \frac{1}{2i}(I^+ S^- - I^- S^+) = I_y S_x - I_x S_y, \quad I_z^{(23)} \equiv \frac{1}{2}(I_z - S_z)$$

Double-quantum space:

$$I_x^{(14)} \equiv \frac{1}{2}(I^+ S^+ + I^- S^-) = I_x S_x - I_y S_y, \quad I_y^{(14)} \equiv \frac{1}{2i}(I^+ S^+ - I^- S^-) = I_y S_x + I_x S_y, \quad I_z^{(14)} \equiv \frac{1}{2}(I_z + S_z)$$

In the literature, these fictitious spin operators are sometimes denoted as $I_x^{(0)}$, I_x^{ZQ} , or $I_x^{(2)}$, I_x^{DQ} , etc. It is usually clear from the context which space we are in.

The fictitious spin-1/2 operators follow the same formal commutation properties as single-spin operators, i.e.

$$\begin{aligned}\left[I_x^{(23)}, I_y^{(23)} \right] &= i I_z^{(23)} \text{ and their cyclic permutations} \\ \left[I_y^{(14)}, I_z^{(14)} \right] &= i I_x^{(14)} \text{ and their cyclic permutations}\end{aligned}$$

Importantly, operators in different spaces always commute: $[I_x^{(0)}, I_y^{(2)}] = 0$, etc.

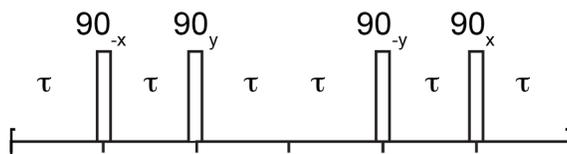
Lectures #3: Understanding Dipolar Decoupling and Recoupling

1. Homonuclear Decoupling

The average Hamiltonian theory was developed initially to understand multiple pulse decoupling sequences. Here rf pulses intersperse with free evolution periods, and one would like to decouple homonuclear dipolar couplings while retaining chemical shift interaction.

1.1 The WAHUHA-4 sequence:

$$\left[\tau - 90^\circ_{-x} - \tau - 90^\circ_y - \tau - \tau - 90^\circ_{-y} - \tau - 90^\circ_x - \tau \right]_n$$



We assume very short (and very hard) pulses and short delays tau. If the pulse length is not negligible (finite pulse length), then the central window with two tau periods should be $2 \times \tau + t_{90^\circ}$.

The density operator at the end of one cycle of this pulse sequence is:

$$\rho(t_0 + 6\tau) = U(6\tau)\rho(t_0)U^{-1}(6\tau)$$

where the propagator U is:

$$U(6\tau) = \overline{L_z P_x L_z P_{-y} L_z L_z P_y L_z P_{-x} L_z}$$

Here the free evolution operator L_z is:

$$L_z = e^{-iHt} = e^{-i(H_{CS} + H_{IS,z} + H_{II,z})t}$$

and the rf pulse propagator is:

$$P_\alpha \equiv e^{-iH_{rf,\alpha}t}$$

Since $H_{rf,\alpha} = -\gamma B_1 I_\alpha$, we obtain

$$P_\alpha = e^{i\gamma B_1 t I_\alpha} = e^{-i\omega_1 t I_\alpha}$$

For 90° pulses, using the sign convention that $\gamma B_1 t = -\omega_1 t = \frac{\pi}{2}$

We obtain

$$P_\alpha = e^{i\frac{\pi}{2} I_\alpha}$$

A pulse of flip angle ϕ rotates the Z Hamiltonian to a different direction based on the left hand rule. This principle is based on the following equation:

$$e^{i\phi I_\alpha} e^{-iH_z t} e^{-i\phi I_\alpha} = \exp\left(e^{i\phi I_\alpha} \cdot (-iH_z t) \cdot e^{-i\phi I_\alpha}\right)$$

Therefore, rotation of an exponential operator is the same as the exponential of the rotation of the operator itself.

Applying the above equation, for example, we obtain:

$$P_x L_z P_x^{-1} = e^{i\frac{\pi}{2} I_x} e^{-iH_z \tau} e^{-i\frac{\pi}{2} I_x} = \exp\left(e^{i\frac{\pi}{2} I_x} \cdot (-iH_z \tau) \cdot e^{-i\frac{\pi}{2} I_x}\right) = \exp(-iH_y \tau) = L_y$$

This means that the pulses act on the free-evolution-period's local Hamiltonian the same way that the pulses act on the spin density operators, except for a sign reversal.

With this principle, we can simplify the propagator $U(6\tau)$ by inserting unit operators $1 = P_\alpha^{-1} P_\alpha$ to rotate the free-evolution operators. Doing this several times eventually shift all the pulse propagators together, separate from the free-evolution operators.

$$\begin{aligned} U(6\tau) &= \overline{L_z P_x L_z P_y L_z L_z P_y L_z P_x L_z} \\ &= L_z P_x L_z \left(P_x^{-1} P_x\right) P_y L_z L_z \left(P_y^{-1} P_y\right) P_x L_z \left(P_x^{-1} P_x\right) P_x L_z \left(P_x^{-1} P_x\right) \\ &= L_z L_y P_x L_x L_x P_y L_x L_x P_y L_x L_x P_x \\ &= L_z L_y L_x L_x P_x P_y L_x \left(P_y^{-1} P_y\right) L_y P_y P_x \\ &= L_z L_y L_x L_x P_x L_z L_y P_y P_x = L_z L_y L_x L_x P_x L_z \left(P_x^{-1} P_x\right) L_y P_y P_x \\ &= L_z L_y L_x L_x L_y P_x L_y P_y P_x = L_z L_y L_x L_x L_y P_x L_y \left(P_x^{-1} P_x\right) P_y P_x \\ &= L_z L_y L_x L_x L_y L_z P_x P_y P_x \end{aligned}$$

With the 4 pulse propagators together, and with the phases of the 4 pulses canceling each other, the combined effect of the 4 pulses is null:

$$P_x P_y P_y P_x = e^{i\frac{\pi}{2} I_x} \underbrace{e^{i\frac{\pi}{2} I_y} e^{i\frac{\pi}{2} I_y}}_1 e^{i\frac{\pi}{2} I_x} = e^{i\frac{\pi}{2} I_x} e^{i\frac{\pi}{2} I_x} = 1$$

So WAHUHA-4 is a cyclic sequence.

Then

$$U(6\tau) = L_z L_y L_x L_x L_y L_z = e^{-iH_z \tau} e^{-iH_y \tau} e^{-iH_x \tau} e^{-iH_x \tau} e^{-iH_y \tau} e^{-iH_z \tau}$$

In the limit of short τ (compared to the inverse of the coupling), we can Taylor-expand the exponentials and obtain

$$U(6\tau) \approx 1 - i\left(H_z + H_y + 2H_x + H_y + H_z\right)\tau \approx e^{-i\bar{H} \cdot 6\tau}$$

where

$$\bar{H} = \left(H_z + H_y + 2H_x + H_y + H_z\right)/6 = \left(H_z + H_y + H_x\right)/3$$

In general, $H_\alpha = H_{CS,\alpha} + H_{IS,\alpha} + H_{II,\alpha} = \omega_I I_\alpha + \omega_{IS} I_\alpha S_z + \omega_{II} (3I_\alpha I_\alpha - I \cdot I)$,

Therefore, $\bar{H} = (H_z + H_y + H_x) / 3$

$$= \frac{1}{3} \omega_I (I_z + I_x + I_y) + \dots (IS \text{ terms}) + \frac{1}{3} \omega_{II} \underbrace{[(3I_z I_z - I \cdot I) + (3I_x I_x - I \cdot I) + (3I_y I_y - I \cdot I)]}_{\text{magic zero}}$$

$$= \frac{1}{3} \omega_I (I_z + I_x + I_y) + (IS \text{ terms}) + 0$$

So the average Hamiltonian of the WAHUHA-4 sequence is:

$$\bar{H} \cdot 6\tau = \frac{1}{3} \omega_I (I_z + I_x + I_y) \cdot 6\tau + (IS \text{ terms}) \cdot 6\tau = \omega_{eff} \cdot \hat{I} \cdot 6\tau + \omega_{eff,IS} \hat{I} S_z \cdot 6\tau$$

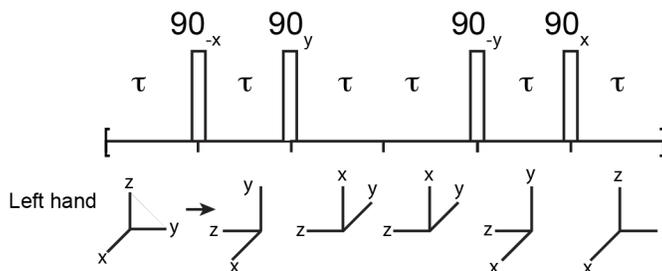
where the effective chemical shift frequency is: $\omega_{eff} = \frac{1}{3} \omega_I \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{3}} \omega_I \cdot \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$
scaling factor

So WAHUHA -4 has a scaling factor of $0.577 = 1/\sqrt{3}$ for both chemical shift and heteronuclear dipolar coupling, and the effective field points along the (1 1 1) diagonal of the cube. We can use WAHUHA-4 and analogous sequences in the DIPSHIFT family of experiments to measure heteronuclear dipolar couplings, with the couplings scaled down by the corresponding factor.

The propagator algebra can be schematically represented using a toggling frame approach:

- 1) flip the interaction frame (the coordinate system) around the axis of the pulses in the rotating frame (left hand rule).
- 2) the axis of the interaction frame coordinate system that is parallel to the z-axis of the rotating frame is the H_1' 's spin operator direction.
- 3) sum up all the H_1' directions to obtain the average Hamiltonian.

For WAHUHA, the toggling frame directions are:



So the interaction frame Hamiltonian directions are:

$$z, y, x, x, y, z$$

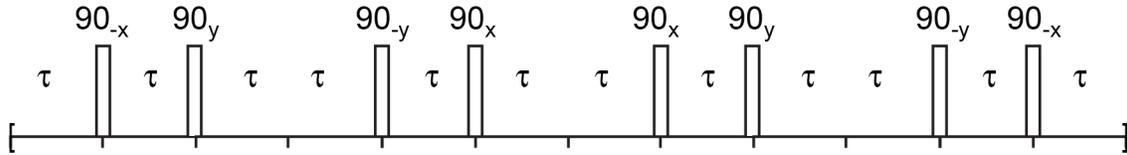
In the rf pulse interaction frame, the effect of the pulses are transformed away. The above result is fully equivalent to the algebra that gave $U(6\tau) = L_z L_y L_x L_x L_y L_z$.

(Verify that this left-hand toggling frame math is equivalent to right-hand rotations in the interaction representation.)

1.2 MREV-8:

MREV-8 is a concatenation of the WHH-4 sequence, with phase inversion of the outer two pulses:

$$\left[\tau - 90^\circ_{-x} - \tau - 90^\circ_y - \tau - \tau - 90^\circ_{-y} - \tau - 90^\circ_x - \tau - \tau - 90^\circ_x - \tau - 90^\circ_{-y} - \tau - \tau - 90^\circ_y - \tau - 90^\circ_{-x} - \tau \right]_n$$

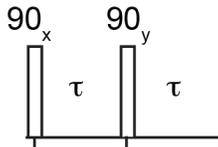


It can be shown that the MREV-8 effective frequency is: $\omega_{eff} = \underbrace{\frac{\sqrt{2}}{3}}_{\text{scaling factor}} \omega_I \cdot \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$.

So the scaling factor is $0.47 = \frac{\sqrt{2}}{3}$, and the effective field points along the diagonal of the xz plane.

2. Quadrupolar Echo (called solid echo for dipolar coupled spin pairs)

$$90^\circ_x - \tau - 90^\circ_y - \tau$$



The quadrupolar Hamiltonian is: $H_{z,Q} = \omega_Q (3I_z^2 - I \cdot I)$

The initial 90° pulse creates $\rho(0) = I_y$.

The propagator of the quad echo sequence is:

$$\begin{aligned} U(2\tau) &= e^{-iH_{z,Q}\tau} e^{i\frac{\pi}{2}I_y} e^{-iH_{z,Q}\tau} = e^{-iH_{z,Q}\tau} e^{i\frac{\pi}{2}I_y} e^{-iH_{z,Q}\tau} \left(e^{-i\frac{\pi}{2}I_y} e^{i\frac{\pi}{2}I_y} \right) \\ &= e^{-i\omega_Q(3I_z^2 - I \cdot I)\tau} e^{-i\omega_Q(3I_x^2 - I \cdot I)\tau} e^{i\frac{\pi}{2}I_y} \\ &= e^{-i\omega_Q(3I_z^2 - I \cdot I)\tau} e^{-i\omega_Q(3I_x^2 - I \cdot I)\tau} I_y e^{i\omega_Q(3I_x^2 - I \cdot I)\tau} e^{i\omega_Q(3I_z^2 - I \cdot I)\tau} \end{aligned}$$

$$\rho(2\tau) = U(2\tau)\rho(0)U^{-1}(2\tau) = e^{-i\omega_Q(3I_z^2 - I \cdot I)\tau} e^{-i\omega_Q(3I_x^2 - I \cdot I)\tau} \underbrace{e^{i\frac{\pi}{2}I_y} I_y e^{-i\frac{\pi}{2}I_y}}_{\text{commute}} e^{i\omega_Q(3I_x^2 - I \cdot I)\tau} e^{i\omega_Q(3I_z^2 - I \cdot I)\tau}$$

To combine the exponents of the product, the two exponents must commute. For spin 1/2 and spin-1 nuclei, the commutation $[I_z^2, I_x^2] = 0$ can be proven easily (also QE also works for half-integer nuclei):

$$\text{For spin-1, } I_z = \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix}, I_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & \\ 1 & 0 & 1 \\ & 1 & 0 \end{pmatrix}, I_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & \\ i & 0 & -i \\ & i & 0 \end{pmatrix}$$

The squares of the first two operators are:

$$I_z^2 = \begin{pmatrix} 1 & & \\ & 0 & \\ & & 1 \end{pmatrix}, I_x^2 = \frac{1}{2} \begin{pmatrix} 1 & & 1 \\ & 2 & \\ 1 & & 1 \end{pmatrix}$$

$$I_z^2 I_x^2 = \begin{pmatrix} 1 & & \\ & 0 & \\ & & 1 \end{pmatrix} \frac{1}{2} \begin{pmatrix} 1 & & 1 \\ & 2 & \\ 1 & & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & & 1 \\ & 2 & \\ 1 & & 1 \end{pmatrix}$$

$$I_x^2 I_z^2 = \frac{1}{2} \begin{pmatrix} 1 & & 1 \\ & 2 & \\ 1 & & 1 \end{pmatrix} \begin{pmatrix} 1 & & \\ & 0 & \\ & & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & & 1 \\ & 2 & \\ 1 & & 1 \end{pmatrix} \quad \text{So } [I_z^2, I_x^2] = 0.$$

Under this commutation condition,

$$\rho(2\tau) = e^{-i\omega_Q(3I_z^2 - I \cdot I + 3I_x^2 - I \cdot I)\tau} I_y e^{i\omega_Q(3I_x^2 - I \cdot I + 3I_z^2 - I \cdot I)\tau} = e^{i\omega_Q(3I_y^2 - I \cdot I)\tau} I_y e^{-i\omega_Q(3I_y^2 - I \cdot I)\tau}$$

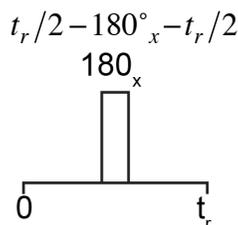
where we invoke the magic zero: $(3I_y^2 - I \cdot I) + (3I_z^2 - I \cdot I) + (3I_x^2 - I \cdot I) = 0$

Since $[3I_y^2 - I \cdot I, I_y] = 0$, we obtain $\rho(2\tau) = I_y = \rho(0)$. \rightarrow an echo forms.

As long as the second 90° pulse is along the magnetization direction (-y will work), we will obtain an echo.

3. Heteronuclear dipolar recoupling under MAS by π pulses – REDOR

This is the first MAS recoupling sequence we analyze. The basic pulse sequence module is:



The propagator is: $U = L_z P_x L_z = e^{-i \int_{t_r/2}^{t_r} H_{IS}(t) dt} e^{-i\pi I_x} e^{-i \int_0^{t_r/2} H_{IS}(t) dt}$.

We know that MAS averages the dipolar coupling, i.e.

$$e^{-i \int_0^{t_r} H_{IS}(t) dt} = 1, \quad \text{or} \quad \int_0^{t_r} H_{IS}(t) dt = 0.$$

Thus, $\int_{t_r/2}^{t_r} H_{IS}(t) dt = \int_0^{t_r} H_{IS}(t) dt - \int_0^{t_r/2} H_{IS}(t) dt = -\int_0^{t_r/2} H_{IS}(t) dt$

Since MAS affects the spatial part of the Hamiltonian, we can write the integral of the Hamiltonian in terms of a dipolar phase ϕ :

$$\int_0^{t_r/2} H_{IS}(t) dt = \int_0^{t_r/2} \omega_{IS}(t) 2I_z S_z dt = \phi_{t_r/2} \cdot 2I_z S_z,$$

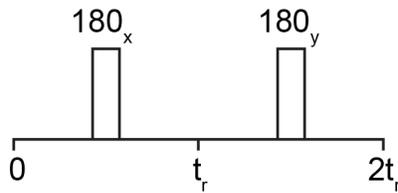
where $\phi_{t_r/2} = \int_0^{t_r/2} \omega_{IS}(t) dt$

Then $U = e^{i\phi_{t_r/2} 2I_z S_z} e^{-i\pi I_x} e^{-i\phi_{t_r/2} 2I_z S_z}$,

$$\begin{aligned} \rho(t_r) &= U \rho(0) U^{-1} = e^{i\phi_{t_r/2} 2I_z S_z} e^{-i\pi I_x} e^{-i\phi_{t_r/2} 2I_z S_z} \rho(0) U^{-1} \\ &= e^{i\phi_{t_r/2} 2I_z S_z} e^{-i\pi I_x} e^{-i\phi_{t_r/2} 2I_z S_z} I_x U^{-1} = e^{i\phi_{t_r/2} 2I_z S_z} e^{-i\pi I_x} e^{-i\phi_{t_r/2} 2I_z S_z} \left(e^{i\pi I_x} e^{-i\pi I_x} \right) I_x U^{-1} \\ &= e^{i\phi_{t_r/2} 2I_z S_z} e^{i\phi_{t_r/2} 2I_z S_z} \underbrace{e^{-i\pi I_x} I_x e^{i\pi I_x}}_{\text{commute}} e^{-i\phi_{t_r/2} 2I_z S_z} e^{-i\phi_{t_r/2} 2I_z S_z} = e^{i2\phi_{t_r/2} 2I_z S_z} I_x e^{-i2\phi_{t_r/2} 2I_z S_z} = I_x \cos 2\phi - 2I_y S_z \sin 2\phi \end{aligned}$$

If we repeat the exact sequence, but use x and y pulses:

$$t_r/2 - 180_x - t_r/2 - t_r/2 - 180_y - t_r/2$$



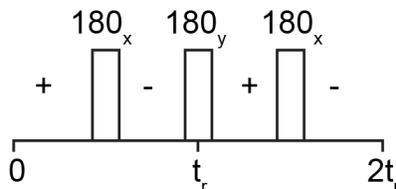
Then:

$$\begin{aligned} \rho(2t_r) &= e^{i2\phi_{t_r/2} 2I_z S_z} e^{i\pi I_y} \rho(t_r) U^{-1} = e^{i2\phi_{t_r/2} 2I_z S_z} e^{i\pi I_y} \left(I_x \cos 2\phi - 2I_y S_z \sin 2\phi \right) U^{-1} \\ &= e^{i2\phi_{t_r/2} 2I_z S_z} \left(-I_x \cos 2\phi - 2I_y S_z \sin 2\phi \right) e^{-i2\phi_{t_r/2} 2I_z S_z} \\ &= -I_x \cos^2 2\phi + 2I_y S_z \cos 2\phi \sin 2\phi - 2I_y S_z \sin 2\phi \cos 2\phi - I_x \sin^2 2\phi = -I_x = -\rho(0) \end{aligned}$$

At the end of two rotor periods, the density operator reverts to the initial condition. **So we created an echo, without any net dipolar recoupling!** This is because the sign of the dipolar phase in the second rotor period cancels that of the first rotor period.

To accumulate the dipolar phase and recouple, we need to add a 180° pulse at the end of the first rotor period, i.e. apply π pulses every half rotor period:

$$t_r/2 - 180^\circ_x - t_r/2 - 180^\circ_y - t_r/2 - 180^\circ_x - t_r/2$$



Then, at the end of the first rotor period, before the second π pulse, we have

$$\rho(t_{r-}) = I_x \cos 2\phi - 2I_y S_z \sin 2\phi$$

Right after the second π pulse,

$$\rho(t_{r+}) = -I_x \cos 2\phi - 2I_y S_z \sin 2\phi$$

Then, the second rotor period imposes the following propagator onto the density operator:

$$\begin{aligned} \rho(2t_r) &= e^{i2\phi 2I_z S_z} e^{i\pi I_x} (-I_x \cos 2\phi - 2I_y S_z \sin 2\phi) e^{-i\pi I_x} e^{-i2\phi 2I_z S_z} \\ &= e^{i2\phi 2I_z S_z} (-I_x \cos 2\phi + 2I_y S_z \sin 2\phi) e^{-i2\phi 2I_z S_z} \\ &= -I_x \cos 2\phi \cos 2\phi + 2I_y S_z \cos 2\phi \sin 2\phi + 2I_y S_z \sin 2\phi \cos 2\phi + I_x \sin 2\phi \sin 2\phi \\ &= -I_x (\cos^2 2\phi - \sin^2 2\phi) + 2I_y S_z \sin 4\phi = -I_x \cos 4\phi + 2I_y S_z \sin 4\phi \end{aligned}$$

So now the dipolar phase is accumulated over 2 rotor periods, rather than being canceled.

The general trend is that for n rotor periods of $2n \times \pi$ pulses that are spaced half a rotor period apart,

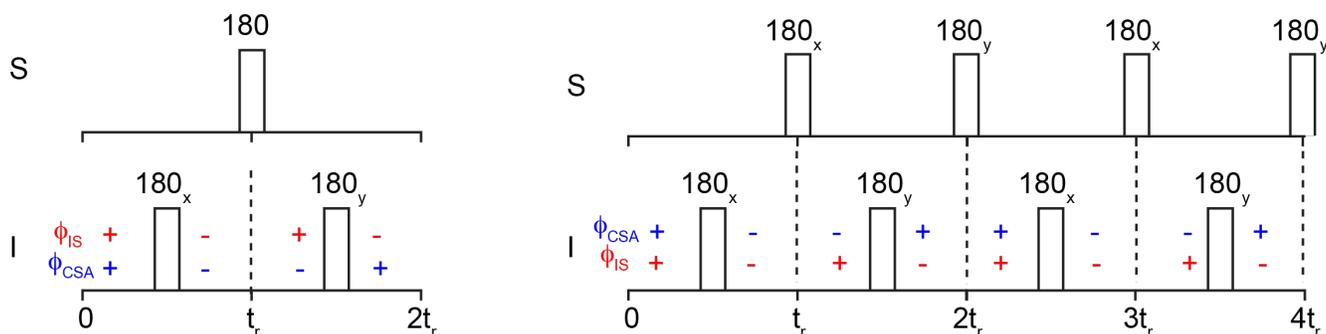
$$\rho(nt_r) = -I_x \cos 2n\phi - 2I_y S_z \sin 2n\phi$$

where $\phi_{t_r/2} = \int_0^{t_r/2} \omega_{IS}(t) dt$.

However, if we use this sequence, we also recouple the I-spin chemical shift anisotropy, with

$$\phi_{CSA} = \int_0^{t_r/2} \omega_I(t) dt .$$

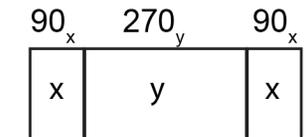
To prevent recoupling of I-spin CSA, we move one I spin π pulse, the one in the middle of the whole pulse train, to the S-spin channel. For IS dipolar coupling, it doesn't matter which channel has the π pulse, as long as there are two π pulses per rotor period on the two channels. But by moving the central π pulse to the S channel, we refocus the S chemical shift evolution, prevent the I-spin CSA recoupling, and retain the IS dipolar recoupling.



4. Phase-Alternating Composite Pulses

So far we applied AHT to either 1) *constant-phase* continuous-irradiation sequences, where the expression for the interaction-representation spin interactions is sinusoidal oscillation, or 2) delta-function windowed pulse sequences, where evolution periods alternate with pulses. For the latter we used the pictorial **toggle frame approach** and the **unit-operator-insertion propagator approach** to determine the average H.

But for phase-alternating windowless pulse sequences, the above algebra does not suffice, and a more formal and complete way of calculating the interaction-representation Hamiltonian is necessary. An example is the composite pulse,



which achieves **broadband population inversion** (i.e. inversion of z-magnetization under resonance offset). See Tycko, Phys Rev Lett, 51 775-777, 1983.

To show that the resonance offset (i.e. chemical shift) Hamiltonian is averaged to 0 to first order, we need to calculate the chemical shift Hamiltonian in the interaction frame of the three successive pulses. Although this sounds the same as what we did for WAHUHA, the fact that the pulses are not delta-function pulses and chemical shift evolution is simultaneous to the pulses calls for a slightly different algebra.

Let's write the propagator for a hypothetical pulse-delay-pulse-delay sequence, and insert the unit operators as before, but in a more suggestive way. The propagator is:

$$\begin{aligned}
U(2\tau) &= \overline{L_z P_2 L_z P_1} = (P_2 P_2^{-1}) L_z P_2 (P_1 P_1^{-1}) L_z P_1 \\
&= P_2 (P_1 P_1^{-1}) P_2^{-1} L_z P_2 P_1 (P_1^{-1} L_z P_1) \\
&= P_2 P_1 \cdot \underbrace{(P_1^{-1} P_2^{-1} L_z P_2 P_1)}_{\text{int rep of the 2nd pulse}} \cdot \underbrace{(P_1^{-1} L_z P_1)}_{\text{int rep of the 1st pulse}}
\end{aligned} \tag{1}$$

So to calculate the interaction representation Hamiltonian under several pulses, we rotate the spin interaction by the pulse immediately before the delay or simultaneous to the spin interaction, and then rotate the interaction by the pulse before that. The order of rotation is the last pulse first and first pulse last, and the sense of rotation is the right hand (verify).

For the WAHUA-4 sequence, the interaction representation Hamiltonians are

$$\begin{array}{l}
\left[\tau - 90^\circ_{-x} - \tau - 90^\circ_y - \tau - \tau - 90^\circ_{-y} - \tau - 90^\circ_x - \tau \right]_n \\
H_z \\
\begin{array}{l}
\text{1st pulse} \rightarrow H_y \\
\text{2nd pulse} \rightarrow \\
\text{3rd pulse} \rightarrow \\
\text{4th pulse} \rightarrow
\end{array}
\end{array} \tag{2}$$

$$\begin{array}{l}
H_x \rightarrow H_x \\
H_{-x} \rightarrow H_z \rightarrow H_y \\
H_{-y} \rightarrow H_z
\end{array}$$

In the composite pulse, during each pulse $H = H_{rf} + H_{cs} = \omega_1 I_x + \omega_{cs} I_z$

The propagator for the composite pulse is then:

$$U = e^{i(\omega_1 I_x + \omega_{cs} I_z)t} e^{i(\omega_1 I_y + \omega_{cs} I_z)3t} e^{i(\omega_1 I_x + \omega_{cs} I_z)t} \tag{3}$$

1st pulse: the chemical shift Hamiltonian in the interaction frame of the rf pulse is:

$$\widetilde{H}_{CS,1} = e^{i\omega_1 I_x t} (\omega_{cs} I_z) e^{-i\omega_1 I_x t} = \omega_{cs} (I_z \cos \omega_1 t - I_y \sin \omega_1 t) \tag{4}$$

The average chemical shift Hamiltonian is:

$$\overline{\widetilde{H}}_{CS,1}^{(0)} = \frac{\omega_{cs}}{t} \int_0^{t=\pi/2\omega_1} dt' (I_z \cos \omega_1 t' - I_y \sin \omega_1 t') = \frac{\omega_{cs}}{\omega_1 t} (I_z - I_y) \tag{5}$$

Note: for simplicity, I have made a sign switch for ω_1 , treating it as the absolute value $|\omega_1|$, so that the prediction from the right-hand rotation for interaction-frame transformation can be directly written into the equation, at the same time this allows (and requires) us to write the equality that $|\omega_1 t| = \pi/2$.

Otherwise, we have to acknowledge that $\omega_1 t = -\pi/2$, and deal with the very cumbersome algebraic juggernaut of:

$\frac{1}{t} \int_0^t +I_y \sin \omega_1 t' dt' = -\frac{1}{\omega_1 t} I_y \cos \omega_1 t' \Big|_0^t = -\frac{1}{\omega_1 t} I_y (0-1) = \frac{1}{-\pi/2} I_y$! Which is the same result as when we treat the frequency in terms of its absolute value (see part of Eq. 5).

2nd pulse:

$$\begin{aligned} \widetilde{H}_{CS,2} &= P_1^{-1} P_2^{-1} (\omega_I I_z) P_2 P_1 = e^{i\frac{\pi}{2} I_x} e^{i\omega_I I_y 3t} (\omega_{CS} I_z) e^{-i\omega_I I_y 3t} e^{-i\frac{\pi}{2} I_x} \\ &= \omega_{CS} e^{i\frac{\pi}{2} I_x} (I_z \cos 3\omega_1 t + I_x \sin 3\omega_1 t) e^{-i\frac{\pi}{2} I_x} = \omega_{CS} (-I_y \cos 3\omega_1 t + I_x \sin 3\omega_1 t) \end{aligned} \quad (6)$$

So $P_2^{-1} H_{CS} P_2$ rotation creates a time-dependent oscillation, while the outer $P_1^{-1} (P_2^{-1} H_{CS} P_2) P_1$ rotation has a fixed phase of 90° .

The average Hamiltonian for the second pulse is:

$$\overline{\widetilde{H}}_{CS,2}^{(0)} = \frac{1}{3t} \omega_{CS} \int_0^{t=\pi/2\omega_1} (-I_y \cos 3\omega_1 t' + I_x \sin 3\omega_1 t') dt' = \frac{\omega_{CS}}{3\omega_1 t} (-I_y(-1) - I_x(-1)) = \frac{\omega_{CS}}{3\omega_1 t} (I_y + I_x) \quad (7)$$

3rd pulse:

$$\begin{aligned} \widetilde{H}_{CS,3} &= P_1^{-1} P_2^{-1} P_3^{-1} (\omega_{CS} I_z) P_3 P_2 P_1 = e^{i\frac{\pi}{2} I_x} e^{i\frac{3\pi}{2} I_y} e^{i\omega_I I_x t} (\omega_{CS} I_z) e^{-i\omega_I I_x t} e^{-i\frac{3\pi}{2} I_y} e^{-i\frac{\pi}{2} I_x} \\ &= \omega_{CS} \cdot e^{i\frac{\pi}{2} I_x} e^{i\frac{3\pi}{2} I_y} (I_z \cos \omega_1 t - I_y \sin \omega_1 t) e^{-i\frac{3\pi}{2} I_y} e^{-i\frac{\pi}{2} I_x} \\ &= \omega_{CS} \cdot e^{i\frac{\pi}{2} I_x} (-I_x \cos \omega_1 t - I_y \sin \omega_1 t) e^{-i\frac{\pi}{2} I_x} = \omega_{CS} \cdot (-I_x \cos \omega_1 t - I_z \sin \omega_1 t) \end{aligned} \quad (8)$$

$$\overline{\widetilde{H}}_{CS,3}^{(0)} = \frac{\omega_{CS}}{t} \int_0^{t=\pi/2\omega_1} (-I_x \cos \omega_1 t' - I_z \sin \omega_1 t') dt' = \frac{\omega_{CS}}{\omega_1 t} (-I_x(1) + I_z(-1)) = \frac{\omega_{CS}}{\omega_1 t} (-I_x - I_z) \quad (9)$$

The average CS Hamiltonian of $90^\circ_x 270^\circ_y 90^\circ_x$ is therefore:

$$\begin{aligned} \overline{\widetilde{H}}_{CS}^{(0)} &= \frac{1}{5t} \left[\overline{\widetilde{H}}_{CS,1}^{(0)} \cdot t + \overline{\widetilde{H}}_{CS,2}^{(0)} \cdot 3t + \overline{\widetilde{H}}_{CS,3}^{(0)} \cdot t \right] \\ &= \frac{1}{5t} \left[\frac{\omega_I}{\omega_1 t} (I_z - I_y) \cdot t + \frac{\omega_I}{3\omega_1 t} (I_y + I_x) \cdot 3t + \frac{\omega_I}{\omega_1 t} (-I_x - I_z) \cdot t \right] \\ &= \frac{1}{5t} \frac{\omega_I}{\omega_1} \left[(I_z - I_y) + (I_y + I_x) + (-I_x - I_z) \right] = 0 \end{aligned} \quad (10)$$

Finally, we consider the density operator evolution under this average Hamiltonian:

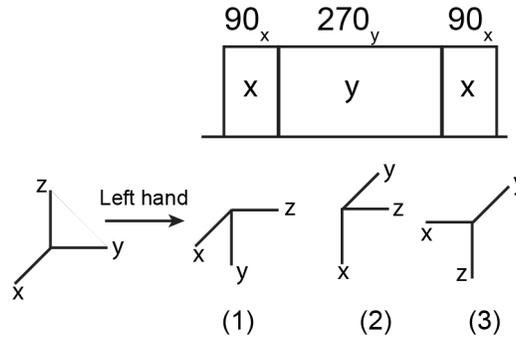
$$\begin{aligned}
 \rho(t) &= U(t) \cdot \rho(0) \cdot U^{-1}(t) = \underbrace{T e^{-iH_{rf}t}}_{U_{rf}(t)} \tilde{U}(t) \cdot \rho(0) \cdot \tilde{U}^{-1}(t) \underbrace{T e^{-iH_{rf}t}}_{U_{rf}^{-1}(t)} \\
 &= U_{rf}(t) \underbrace{e^{-i\bar{H}Cst}}_1 \cdot \rho(0) \cdot e^{i\bar{H}Cst} U_{rf}(t) = P_3 P_2 P_1 \cdot \rho(0) \cdot P_1 P_2 P_3 \\
 &= e^{-i\frac{\pi}{2}I_x} e^{-i\frac{3\pi}{2}I_y} e^{-i\frac{\pi}{2}I_x} \cdot \rho(0) \cdot e^{i\frac{\pi}{2}I_x} e^{i\frac{3\pi}{2}I_y} e^{i\frac{\pi}{2}I_x}
 \end{aligned} \tag{11}$$

When $\rho(0) = I_z$, the successive rotation by the three pulses produces (Left Hand) $\rho(0) = I_z \rightarrow I_y \rightarrow I_y \rightarrow \rho(t) = -I_z$.

But if the initial density operator is in the transverse plane, e.g. $\rho(0) = I_x$, then no inversion is achieved: $\rho(0) = I_x \rightarrow I_x \rightarrow -I_z \rightarrow \rho(t) = -I_y$.

So this broadband inversion composite pulse works only for z-magnetization, e.g. in REDOR sequences, but not for transverse magnetization.

Alternatively, we can also use the toggling frame to analyze the composite pulse. **Key: the ending coordinate-system orientation of the preceding pulse is the starting orientation of the next pulse.**



The axis of the toggling-frame Hamiltonian along the rotating-frame z-axis indicates the sine component of the oscillation (after the pulse flip angle), while the initial operator direction from the last step of the transformation gives the cosine component:

1st pulse: start with z, end with $-y$ after 90° rotation:

$$H_{tog,1} = \omega_I \left(I_z \cos \omega_1 t - I_y \sin \omega_1 t \right) \text{ for } t = 0 \text{ to } t = \frac{\pi/2}{\omega_1}, \quad \bar{H}_{tog,1} = \frac{\omega_I}{\omega_1 t} (I_z - I_y)$$

2nd pulse: start with $-y$, end with $-x$ after 270° rotation:

$$H_{tog,2} = \omega_I \left(-I_y \cos 3\omega_1 t + I_x \sin 3\omega_1 t \right) \text{ for } t = 0 \text{ to } t = \frac{\pi/2}{\omega_1}, \quad \bar{H}_{tog,2} = \frac{\omega_I}{3\omega_1 t} (I_y + I_x)$$

3rd pulse: start with $-x$, end with $-z$ after 90° rotation:

$$H_{tog,3} = \omega_I \left(-I_x \cos \omega_1 t - I_z \sin \omega_1 t \right) \text{ for } t = 0 \text{ to } t = \frac{\pi/2}{\omega_1}, \quad \bar{H}_{tog,3} = \frac{\omega_I}{\omega_1 t} (-I_x - I_z)$$

Average Hamiltonian:

$$\overline{H}_{togg}^{(0)} = \frac{1}{5t} \left(\overline{H}_{togg,1} \cdot t + \overline{H}_{togg,2} \cdot 3t + \overline{H}_{togg,3} \cdot t \right) = \frac{\omega_I}{5\omega_1 t} (I_z - I_y + I_y + I_x - I_x - I_z) = 0$$