Average Hamiltonian Theory and Recoupling

1) Simple example of AHT #1: WAHUHA sequence with delta-function pulses

2) Simple example of AHT #2: Hartmann-Hahn matching in cross-polarization

3) General formalism of average Hamiltonian theory

4) General idea of recoupling under magic-angle spinning
   a) CSA recoupling by rotor-synchronized $\pi$ pulses
   b) Homonuclear dipolar recoupling by delta-function $\pi/2$ pulses (DRAMA)
   c) Homonuclear dipolar recoupling by continuous irradiation (HORROR)

(see also: tycko_2018_lecture1.pdf and tycko_recoupling_notes5.pdf)

(R. Tycko, 2020 Winter School on Biomolecular Solid State NMR)
1) Simple example of AHT #1: WAHUHA sequence with delta-function pulses

\[
\tau \quad \tau \quad 2\tau \quad \tau \quad \tau
\]

\[
H = H_{RF}(t) + H_{dip} + H_{CS}
\]

\[
= H_{RF}(t) + d(S_{z1}S_{z2} - \frac{1}{3}S_{z1}\cdot S_{z2}) + (\delta_1S_{z1} + \delta_2S_{z2})
\]

\[
= H_{RF}(t) + V_{zz}
\]

two-spin system, no MAS:

What is the evolution operator for this pulse sequence? The Hamiltonian is piecewise-constant, and the pulses are very strong, so we can ignore V during the pulses:

\[
U(6\tau) = e^{-iV_{zz}\tau}R_x(-\frac{\pi}{2})e^{-iV_{zz}\tau}R_y(\frac{\pi}{2})e^{-2iV_{zz}\tau}R_y(-\frac{\pi}{2})e^{-iV_{zz}\tau}R_x(\frac{\pi}{2})e^{-iV_{zz}\tau}
\]

Use a trick:

\[
U(6\tau) = e^{-iV_{zz}\tau}R_x(-\frac{\pi}{2})e^{-iV_{zz}\tau}R_x(\frac{\pi}{2})R_x(-\frac{\pi}{2})R_y(\frac{\pi}{2})e^{-2iV_{zz}\tau}R_y(-\frac{\pi}{2})R_x(\frac{\pi}{2})R_x(-\frac{\pi}{2})e^{-iV_{zz}\tau}R_x(\frac{\pi}{2})e^{-iV_{zz}\tau}
\]

1 1
1) Simple example of AHT #1: WAHUHA sequence with delta-function pulses

\[ H = H_{RF}(t) + H_{dip} + H_{CS} \]

\[ = H_{RF}(t) + d(S_{z1}S_{z2} - \frac{1}{3} \mathbf{S}_1 \cdot \mathbf{S}_2) + (\delta_1 S_{z1} + \delta_2 S_{z2}) \]

\[ = H_{RF}(t) + V_{zz} \]

Now the evolution operator contains these groups of terms:

\[ U(6\tau) = e^{-iV_{xx}\tau} e^{-iV_{yy}\tau} R_x(\frac{-\pi}{2}) e^{-2iV_{zz}\tau} R_y(\frac{-\pi}{2}) R_x(\frac{\pi}{2}) e^{-iV_{yy}\tau} e^{-iV_{zz}\tau} \]

Use another trick: \( A e^B A^{-1} = e^{ABA^{-1}} \) and recall that \( R_x(\frac{-\pi}{2})S_z R_x(\frac{\pi}{2}) = S_y \)

Also, \( R_x(\frac{-\pi}{2})\mathbf{S}_1 \cdot \mathbf{S}_2 R_x(\frac{\pi}{2}) = \mathbf{S}_1 \cdot \mathbf{S}_2 \)

Therefore:

\[ U(6\tau) = e^{-iV_{xx}\tau} e^{-iV_{yy}\tau} R_x(\frac{-\pi}{2}) e^{-2iV_{zz}\tau} R_y(\frac{-\pi}{2}) e^{-iV_{yy}\tau} e^{-iV_{zz}\tau} \]

with \( V_{xx} = d(S_{x1}S_{x2} - \frac{1}{3} \mathbf{S}_1 \cdot \mathbf{S}_2) + (\delta_1 S_{x1} + \delta_2 S_{x2}) \)

and \( V_{yy} = d(S_{y1}S_{y2} - \frac{1}{3} \mathbf{S}_1 \cdot \mathbf{S}_2) + (\delta_1 S_{y1} + \delta_2 S_{y2}) \)

Finally:

\[ U(6\tau) = e^{-iV_{xx}\tau} e^{-iV_{yy}\tau} e^{-2iV_{xx}\tau} e^{-iV_{yy}\tau} e^{-iV_{zz}\tau} \]

Notice that the RF pulses have vanished! And the dipole-dipole coupling and chemical shift have become time-dependent!

(This is an interaction representation, sometimes called a "toggling frame".)
1) Simple example of AHT #1: WAHUHA sequence with delta-function pulses

\[
\begin{align*}
\tau & \quad \tau & \quad 2\tau & \quad \tau & \quad \tau \\
V_{zz} & \quad V_{yy} & \quad V_{xx} & \quad V_{yy} & \quad V_{zz}
\end{align*}
\]

Now notice that \([V_{xx}, V_{yy}] \neq 0\) \([V_{yy}, V_{zz}] \neq 0\) \([V_{zz}, V_{xx}] \neq 0\) , so it is not true that

\[
U(6\tau) = e^{-iV_{zz}\tau}e^{-iV_{yy}\tau}e^{-2iV_{xx}\tau}e^{-iV_{yy}\tau}e^{-iV_{zz}\tau}
\]

\[= e^{-i2(V_{xx}+V_{yy}+V_{zz})\tau}\]

However, it is approximately true for small \(\tau\):

\[
U(6\tau) = e^{-i2(V_{xx}+V_{yy}+V_{zz})\tau} = e^{-iV_{ave}(6\tau)}
\]

\[V_{ave} = \frac{1}{3}(V_{xx} + V_{yy} + V_{zz})\]

Moreover, \((S_{x1}S_{x2} - \frac{1}{3}S_{z1}\cdot S_{z2}) + (S_{y1}S_{y2} - \frac{1}{3}S_{z1}\cdot S_{z2}) + (S_{z1}S_{z2} - \frac{1}{3}S_{z1}\cdot S_{z2}) = 0\) , so that

\[V_{ave} = \frac{1}{3}\delta_1(S_{x1} + S_{y1} + S_{z1}) + \frac{1}{3}\delta_2(S_{x2} + S_{y2} + S_{z2})\]

The WAHUHA sequence produces an average Hamiltonian in which the dipole-dipole coupling vanishes and the chemical shift is scaled down by a factor of \(\sqrt{3}\) .
2) Simple example of AHT #2: Hartmann-Hahn matching in cross-polarization

**Heteronuclear two-spin system, no MAS.** The Hamiltonian during the cross-polarization contact period is: \( H = H_{RF} + H_{dip} = \omega_I I_x + \omega_S S_x + d I_z S_z \)

What is the Hamiltonian in an interaction representation with respect to \( H_{RF} \)?

As explained yesterday evening, if the total Hamiltonian is \( H = H_0 + V \), then the Hamiltonian in the interaction representation with respect to \( H_0 \) is

\[
\tilde{V}(t) = U_{0}(t)^{-1} V U_{0}(t) .
\]

Applying this to the cross-polarization problem:

\[
\tilde{V}(t) = e^{i(\omega_I I_x + \omega_S S_x) t} (d I_z S_z) e^{-i(\omega_I I_x + \omega_S S_x) t} = d \left( e^{i \omega_I I_x t} I_z e^{-i \omega_I I_x t} \right) \left( e^{i \omega_S S_x t} S_z e^{-i \omega_S S_x t} \right)
\]

\[
= d \left( I_z \cos \omega_I t + I_y \sin \omega_I t \right) \left( S_z \cos \omega_S t + S_y \sin \omega_S t \right)
\]

\[
= \frac{1}{2} d \left\{ I_z S_z [\cos(\omega_I - \omega_S) t + \cos(\omega_I + \omega_S) t] + I_y S_y [\cos(\omega_I - \omega_S) t - \cos(\omega_I + \omega_S) t] + I_y S_z [\sin(\omega_I + \omega_S) t - \sin(\omega_I - \omega_S) t] + I_y S_y [\sin(\omega_I + \omega_S) t + \sin(\omega_I - \omega_S) t] \right\}
\]

The time average of \( \tilde{V}(t) \) is zero unless \( \omega_I = \pm \omega_S \). Then the average coupling becomes \( \frac{1}{2} d (I_z S_z \pm I_y S_y) \). This is the H-H matching condition (without MAS)!
2) Simple example of AHT #2: Hartmann-Hahn matching in cross-polarization

Why is Hartmann-Hahn matching necessary? Why should we create $\frac{1}{2}d(I_zS_z \pm I_yS_y)$? The goal is to transfer polarization from spin $I$ to spin $S$. In other words, starting with a density operator $\rho(0) \propto I_x$, the goal is to create a non-zero expectation value of $S_x$.

$$\langle S_x \rangle = \text{Tr}\{S_x\rho(t)\} = \text{Tr}\{S_xU(t)\rho(0)U(t)^{-1}\} = \text{Tr}\{S_xe^{-iHt}I_xe^{iHt}\}$$

Now, if $H = dI_zS_z$ it can be shown that $\langle S_x \rangle = 0$.

One way to prove this is to use the general fact that $\text{Tr}\{RAR^{-1}\} = \text{Tr}\{A\}$ for any rotation operator $R$. (The trace is invariant to any unitary transformation.) For example, let $R = e^{-iI_x\pi}e^{-iS_y\pi}$. Then

$$\langle S_x \rangle = \text{Tr}\{RS_xe^{-idI_zS_zt}I_xe^{idI_zS_zt}R^{-1}\} = \text{Tr}\{(-S_x)e^{-idI_zS_zt}I_xe^{idI_zS_zt}\} = -\langle S_x \rangle.$$ 

On the other hand, if $H = \frac{1}{2}d(I_zS_z \pm I_yS_y)$, the same proof does not work, because there is no rotation that leaves the Hamiltonian unchanged, changes the sign of $S_x$, and leaves $I_x$ unchanged. Therefore, $\langle S_x \rangle$ is not necessarily zero, and polarization transfer can happen.
3) General formalism of average Hamiltonian theory

Average Hamiltonian Theory describes how a pulse sequence, represented by an RF Hamiltonian $H_{RF}(t)$ in the rotating frame, affects other nuclear spin interactions, represented by a term such as $V(t)$, especially in the limit that the strength of the RF pulses exceeds the strength of other nuclear spin interactions.

AHT works by separating the overall evolution operator $U(t)$ into a product of $U_{RF}(t)$, due to the RF pulses, and $\tilde{U}_{V}(t)$, due to other interactions. In other words, AHT uses an interaction representation with respect to $H_{RF}(t)$ and asks what the effective, time-independent Hamiltonian is in this interaction representation. The effective Hamiltonian is calculated with the Magnus expansion, in which the lowest-order term is simply the time-average of the Hamiltonian in the interaction representation.

Strictly speaking, AHT applies to Hamiltonians that are periodic and pulse sequences that are cyclic. This means that $H(t) = H(t+\tau_c)$, where $\tau_c$ is the repetition period or “cycle time” of the pulse sequence, and $U_{RF}(\tau_c) = 1$. In other words, the RF pulses cancel themselves out at multiples of $\tau_c$. Then, at multiples of $\tau_c$, the interaction representation coincides with the normal rotating frame, and the effective Hamiltonian (usually the average Hamiltonian) completely determines the NMR signals.
3) General formalism of average Hamiltonian theory

\[ H(t) = H_{RF}(t) + V(t) \]
\[ H(t) = H(t + \tau_c) \]
\[ U(t) = U_{RF}(t)\tilde{U}_V(t) \]

\[ U_{RF}(\tau_c) = 1 \implies U(\tau_c) = \tilde{U}_V(\tau_c) \]

\[ \tilde{V}(t) = U_{RF}(t)^{-1} V(t) U_{RF}(t) \implies \tilde{V}(t) = \tilde{V}(t + \tau_c) \]

\[ \tilde{U}_V(\tau_c) = \exp(-iV_{\text{eff}}\tau_c) \quad V_{\text{eff}} = \tilde{V}^{(0)} + \tilde{V}^{(1)} + \tilde{V}^{(2)} + \ldots \]

\[ U(n\tau_c) = \tilde{U}_V(n\tau_c) = [\tilde{U}_V(\tau_c)]^n = \exp(-iV_{\text{eff}}n\tau_c) \quad \rho(n\tau_c) = e^{-iV_{\text{eff}}n\tau_c} \rho(0)e^{iV_{\text{eff}}n\tau_c} \]

\[ \tilde{V}^{(0)} = \frac{1}{\tau_c} \int_0^{\tau_c} dt\tilde{V}(t) \quad \tilde{V}^{(1)} = \frac{-i}{2\tau_c} \int_0^{\tau_c} dt\int_0^t dt'[\tilde{V}(t),\tilde{V}(t')] \]

\[ \tilde{V}^{(2)} = \frac{1}{6\tau_c} \int_0^{\tau_c} dt\int_0^t dt'\int_0^{t''} dt''\{[\tilde{V}(t),[\tilde{V}(t'),\tilde{V}(t'')] + [\tilde{V}(t''),[\tilde{V}(t'),\tilde{V}(t)]]\} \]
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4) General idea of recoupling under magic-angle spinning

Pneumatically-driven sample rotation about $\theta_m$ averages dipole-dipole couplings and chemical shift anisotropies to zero.
4) General idea of recoupling under magic-angle spinning

\[ H_{\text{dip}}(t) = \{ A(\alpha, \beta) \cos(\omega_R t + \gamma) + B(\alpha, \beta) \sin(\omega_R t + \gamma) + C(\alpha, \beta) \cos(2\omega_R t + 2\gamma) \]
\[ + D(\alpha, \beta) \sin(2\omega_R t + 2\gamma) \} \times (S_{z1}S_{z2} - \frac{1}{3}S_1 \cdot S_2) \]

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

Oscillations at \( \omega_R \) and \( 2\omega_R \) make dipole-dipole couplings and CSA average to zero under MAS.
4) General idea of recoupling under magic-angle spinning

But if you apply a periodic, cyclic pulse sequence with $\tau_c$ equal to a multiple of the MAS rotation period $\tau_R$, then you can apply average Hamiltonian theory:

$$H_{\text{dip}}(t) \rightarrow \tilde{H}_{\text{dip}}(t) = \{A(\alpha, \beta)\cos(\omega_R t + \gamma) + B(\alpha, \beta)\sin(\omega_R t + \gamma) + C(\alpha, \beta)\cos(2\omega_R t + 2\gamma)$$

$$+ D(\alpha, \beta)\sin(2\omega_R t + 2\gamma)\} \times [\tilde{S}_{z1}(t)\tilde{S}_{z2}(t) - \frac{1}{3}\tilde{S}_{1}(t)\cdot\tilde{S}_{2}(t)]$$

with $\tilde{S}_{\alpha1}(t) = U_{RF}(t)^{-1}S_{\alpha1}(t)U_{RF}(t)$  $\tilde{S}_{\alpha2}(t) = U_{RF}(t)^{-1}S_{\alpha2}(t)U_{RF}(t)$  $\alpha = x, y, z$

Then, if $[\tilde{S}_{z1}(t)\tilde{S}_{z2}(t) - \frac{1}{3}\tilde{S}_{1}(t)\cdot\tilde{S}_{2}(t)]$ contains terms that oscillate at $\omega_R$ or $2\omega_R$, the average dipole-dipole coupling will not be zero: $H_{\text{dip}}^{(0)} = \frac{1}{\tau_c}\int_0^{\tau_c} dt\tilde{H}_{\text{dip}}(t) \neq 0$

Similarly, if $\tilde{S}_z(t)$ contains terms that oscillate at $\omega_R$ or $2\omega_R$, the average CSA will not be zero: $H_{\text{CSA}}^{(0)} = \frac{1}{\tau_c}\int_0^{\tau_c} dt\tilde{H}_{\text{CSA}}(t) \neq 0$  **This is dipolar recoupling or CSA recoupling.**
4a) CSA recoupling by rotor-synchronized $\pi$ pulses

\[ U_{RF}(t) = \begin{cases} 
    e^{-iS_x \pi}, & 0 < t < \tau_s \\
    e^{iS_x \pi} e^{-iS_x \pi} = 1, & \tau_s < t < \tau_R 
\end{cases} \]

\[ \tilde{S}_z(t) = U_{RF}(t)^{-1}S_z U_{RF}(t) = \begin{cases} 
    -S_z, & 0 < t < \tau_s \\
    +S_z, & \tau_s < t < \tau_R 
\end{cases} \]

\[ \tilde{H}_{\text{CSA}}(t) = \{A'(\alpha, \beta) \cos(\omega_R t + \gamma) + B'(\alpha, \beta) \sin(\omega_R t + \gamma) + C'(\alpha, \beta) \cos(2\omega_R t + 2\gamma) + D'(\alpha, \beta) \sin(2\omega_R t + 2\gamma)\} \times \tilde{S}_z(t) \]

\[ \tilde{H}_{\text{CSA}}^{(0)} = \frac{1}{\tau_R} \int_0^{\tau_R} dt \ \tilde{H}_{\text{CSA}}(t) = \frac{S_z}{\tau_R} \left\{ A' \left[ -\int_0^{\tau_s} dt \cos(\omega_R t + \gamma) + \int_{\tau_s}^{\tau_R} dt \cos(\omega_R t + \gamma) \right] + B' \left[ -\int_0^{\tau_s} dt \sin(\omega_R t + \gamma) + \int_{\tau_s}^{\tau_R} dt \sin(\omega_R t + \gamma) \right] + C' \left[ -\int_0^{\tau_s} dt \cos(2\omega_R t + 2\gamma) + \int_{\tau_s}^{\tau_R} dt \cos(2\omega_R t + 2\gamma) \right] + D' \left[ -\int_0^{\tau_s} dt \sin(2\omega_R t + 2\gamma) + \int_{\tau_s}^{\tau_R} dt \sin(2\omega_R t + 2\gamma) \right] \right\} \]
4a) CSA recoupling by rotor-synchronized $\pi$ pulses

\[ \tilde{H}_{CSA}^{(0)} = \frac{S_z}{2\pi} \{2A'[\sin \gamma - \sin(\phi_s + \gamma)] + 2B'[\cos(\phi_s + \gamma) - \cos \gamma] 
+ C'[\sin 2\gamma - \sin(2\phi_s + 2\gamma)] + D'[\cos(2\phi_s + 2\gamma) - \cos 2\gamma] \}
\]

This is not zero, provided that $\phi_s$ is not 0 or $2\pi$.

How does this compare with the CSA in a non-spinning sample?

In a non-spinning sample (i.e., $\omega_R = 0$),

\[ H_{CSA} = \{A'(\alpha, \beta) \cos \gamma + B'(\alpha, \beta) \sin \gamma + C'(\alpha, \beta) \cos 2\gamma + D'(\alpha, \beta) \sin 2\gamma \} \times S_z \]

This is not the same as $\tilde{H}_{CSA}^{(0)}$, so the orientation dependence of the chemical shift is not the same. The recoupled CSA powder pattern lineshapes are different.

But if $\phi_s \ll 1$, then $\sin(\phi_s + \gamma) \approx \sin \gamma + \phi_s \cos \gamma$, $\cos(\phi_s + \gamma) \approx \cos \gamma - \phi_s \sin \gamma$, $\sin(2\phi_s + 2\gamma) \approx \sin 2\gamma + 2\phi_s \cos 2\gamma$, and $\cos(2\phi_s + 2\gamma) \approx \cos 2\gamma - 2\phi_s \sin 2\gamma$.

This implies that $\tilde{H}_{CSA}^{(0)} \approx \frac{\phi_s}{\pi} H_{CSA}$ when the spacing between $\pi$ pulses is small.
4b) Homonuclear dipolar recoupling by delta-function $\pi/2$ pulses (DRAMA)

$$
\begin{align*}
U_{RF}(t) &= \begin{cases} 
  e^{-iS_x\pi/2}, & 0 < t < \tau_s \\
  e^{iS_x\pi/2} e^{-iS_x\pi/2}, & 1, \tau_s < t < \tau_R 
\end{cases} \\
\tilde{S}_{zj}(t) &= U_{RF}(t)^{-1}S_{zj}U_{RF}(t) = \begin{cases} 
  S_{yj}, & 0 < t < \tau_s \\
  S_{zj}, & \tau_s < t < \tau_R 
\end{cases}
\end{align*}
$$

$$
\tilde{H}_{dip}(t) = \{A \cos(\omega_R t + \gamma) + B \sin(\omega_R t + \gamma) + C \cos(2\omega_R t + 2\gamma) + \sin(2\omega_R t + 2\gamma)\} \\
\times [\tilde{S}_{z1}(t)\tilde{S}_{z2}(t) - \frac{1}{3}\tilde{S}_1(t)\cdot\tilde{S}_2(t)]
$$

$$
\tilde{H}_{dip}^{(0)} = \frac{S_{y1}S_{y2}}{\tau_R} \{A\int_{0}^{\tau_s} dt \cos(\omega_R t + \gamma) + B\int_{0}^{\tau_s} dt \sin(\omega_R t + \gamma) \\
+ C\int_{0}^{\tau_s} dt \cos(2\omega_R t + 2\gamma) + D\int_{0}^{\tau_s} dt \sin(2\omega_R t + 2\gamma)\} \\
+ \frac{S_{z1}S_{z2}}{\tau_R} \{A\int_{\tau_s}^{\tau_R} dt \cos(\omega_R t + \gamma) + B\int_{\tau_s}^{\tau_R} dt \sin(\omega_R t + \gamma) \\
+ C\int_{\tau_s}^{\tau_R} dt \cos(2\omega_R t + 2\gamma) + D\int_{\tau_s}^{\tau_R} dt \sin(2\omega_R t + 2\gamma)\}
$$

As long as the same rotations are applied to both spins, the scalar product $S_{z1}\cdot S_{z2}$ does not change. Therefore, this part of $H_{dip}$ is not recoupled.
Homonuclear dipolar recoupling by delta-function $\pi/2$ pulses (DRAMA)

$$
\tilde{\mathbf{H}}_{\text{dip}}^{(0)} = \frac{1}{2\pi} \{ A[\sin(\phi_s + \gamma) - \sin \gamma] - B[\cos(\phi_s + \gamma) - \cos \gamma]
+ \frac{1}{2} C[\sin(2\phi_s + 2\gamma) - \sin 2\gamma] + \frac{1}{2} D[\cos(2\phi_s + 2\gamma) - \cos 2\gamma] \} \times (S_1 S_2 - S_{z1} S_{z2})
$$

Again, the dipolar powder pattern lineshape depends on $\phi_s$.

4b) Homonuclear dipolar recoupling by delta-function $\pi/2$ pulses (DRAMA)

\[ \tilde{H}_{\text{dip}}^{(0)} = \frac{1}{2\pi} \{ A[\sin(\phi_s + \gamma) - \sin \gamma] - B[\cos(\phi_s + \gamma) - \cos \gamma] \]

\[ + \frac{1}{2} C[\sin(2\phi_s + 2\gamma) - \sin 2\gamma] + \frac{1}{2} D[\cos(2\phi_s + 2\gamma) - \cos 2\gamma] \} \times (S_{y1}S_{y2} - S_{z1}S_{z2}) \]

Also, the recoupled operator $S_{y1}S_{y2} - S_{z1}S_{z2}$ is different from $S_{z1}S_{z2} - \frac{1}{3}S_{z1} \cdot S_{z2}$.

In particular, $[S_{z1}S_{z2} - \frac{1}{3}S_{z1} \cdot S_{z2}, S_{z1} + S_{z2}] = 0$, but $[S_{y1}S_{y2} - S_{z1}S_{z2}, S_{z1} + S_{z2}] \neq 0$.

\[ \tilde{H}_{\text{dip}}^{(0)} = \frac{1}{4\pi} \{ \cdots \} \times [(S_{y1}S_{y2} - S_{z1}S_{z2}) + (S_{x1}S_{x2} - S_{z1}S_{z2})] \]

This longer recoupling sequence has

\[ = -\frac{3}{4\pi} \{ \cdots \} \times (S_{z1}S_{z2} - \frac{1}{3}S_{z1} \cdot S_{z2}) \]
4c) Homonuclear dipolar recoupling by continuous irradiation (HORROR)

\[ U_{RF}(t) = e^{-i\omega_1 S_x t}, \ 0 < t < n\tau_R \]  
(Must have \( n\omega_1 = m\omega_R \) for a cyclic "sequence".)

\[ \tilde{S}_{zj}(t) = U_{RF}^{-1}(t) S_{zj} U_{RF}(t) = S_{zj} \cos \omega_1 t + S_{yj} \sin \omega_1 t \]

\[ \tilde{S}_{z1}(t)\tilde{S}_{z2}(t) = S_{z1} S_{z2} \cos^2 \omega_1 t + S_{y1} S_{y2} \sin^2 \omega_1 t + (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin \omega_1 t \cos \omega_1 t \]

\[ = \frac{1}{2} S_{z1} S_{z2} (1 + \cos 2\omega_1 t) + \frac{1}{2} S_{y1} S_{y2} (1 - \cos 2\omega_1 t) + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin 2\omega_1 t \]

\[ = \frac{1}{2} (S_{z1} S_{z2} + S_{y1} S_{y2}) + \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos 2\omega_1 t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin 2\omega_1 t \]

This means that \( \tilde{H}_{dip}^{(0)} \neq 0 \) only if \( \omega_1 = \omega_R \) or \( \omega_1 = \frac{1}{2} \omega_R \).
4c) Homonuclear dipolar recoupling by continuous irradiation (HORROR)

\[
\tilde{H}_{\text{dip}}^{(0)}(t) = \frac{1}{2\tau_R} \int_0^{2\tau_R} dt \left\{ A \cos(\omega_R t + \gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos \omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin \omega_R t \right] \\
+ B \sin(\omega_R t + \gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos \omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin \omega_R t \right] \right\}
\]

\[
= \frac{1}{2} A [(S_{z1} S_{z2} - S_{y1} S_{y2}) \cos \gamma - (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin \gamma] \\
+ \frac{1}{2} B [(S_{z1} S_{z2} - S_{y1} S_{y2}) \sin \gamma + (S_{z1} S_{y2} + S_{y1} S_{z2}) \cos \gamma]
\]

\[
= \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2})(A \cos \gamma + B \sin \gamma) + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2})(B \cos \gamma - A \sin \gamma)
\]

\[
\tilde{H}_{\text{dip}}^{(0)}(t) = \frac{1}{\tau_R} \int_0^{\tau_R} dt \left\{ C \cos(2\omega_R t + 2\gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos 2\omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin 2\omega_R t \right] \\
+ D \sin(2\omega_R t + 2\gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos 2\omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin 2\omega_R t \right] \right\}
\]

\[
= \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2})(C \cos 2\gamma + D \sin 2\gamma) + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2})(C \cos 2\gamma - D \sin 2\gamma)
\]

If \( \omega_1 = \frac{1}{2} \omega_R \):

\[
\tilde{H}_{\text{dip}}^{(0)}(t) = \frac{1}{2\tau_R} \int_0^{2\tau_R} dt \left\{ A \cos(\omega_R t + \gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos \omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin \omega_R t \right] \\
+ B \sin(\omega_R t + \gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos \omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin \omega_R t \right] \right\}
\]

\[
= \frac{1}{2} \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos \gamma - (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin \gamma \right] \\
+ \frac{1}{2} \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \sin \gamma + (S_{z1} S_{y2} + S_{y1} S_{z2}) \cos \gamma \right]
\]

\[
= \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2})(A \cos \gamma + B \sin \gamma) + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2})(B \cos \gamma - A \sin \gamma)
\]

If \( \omega_1 = \omega_R \):

\[
\tilde{H}_{\text{dip}}^{(0)}(t) = \frac{1}{\tau_R} \int_0^{\tau_R} dt \left\{ C \cos(2\omega_R t + 2\gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos 2\omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin 2\omega_R t \right] \\
+ D \sin(2\omega_R t + 2\gamma) \left[ \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2}) \cos 2\omega_R t + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2}) \sin 2\omega_R t \right] \right\}
\]

\[
= \frac{1}{2} (S_{z1} S_{z2} - S_{y1} S_{y2})(C \cos 2\gamma + D \sin 2\gamma) + \frac{1}{2} (S_{z1} S_{y2} + S_{y1} S_{z2})(C \cos 2\gamma - D \sin 2\gamma)
\]
4c) Homonuclear dipolar recoupling by continuous irradiation (HORROR)

Under both recoupling conditions, \( \tilde{H}_{\text{dip}}^{(0)} \) has the property that \( \text{Tr}\{[\tilde{H}_{\text{dip}}^{(0)}]^2\} \) does not depend on the \( \gamma \) angle. This is called "gamma encoded" recoupling.

This property leads to dipolar powder patterns with sharp "horns", which in turn leads to relatively high polarization transfer efficiencies or double-quantum filtering efficiencies.

Finally, because \( \tilde{S}_z(t) = S_z \cos \omega_1 t + S_y \sin \omega_1 t \), CSA is recoupled when \( \omega_1 = \omega_R \) but not when \( \omega_1 = \frac{1}{2} \omega_R \). Therefore, the \( \omega_1 = \frac{1}{2} \omega_R \) condition is generally preferred.

There are many other aspects of recoupling that I have not covered in this lecture: symmetry-based recoupling, second-order recoupling, constant-time recoupling, frequency-selective or band-selective recoupling, etc., etc.