A) Averaging – Magic angle sample spinning

B) Polarization transfer - CP
Interactions in solid state

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Order of Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeeman</td>
<td>$10^8$ Hz</td>
</tr>
<tr>
<td>Chemical Shift</td>
<td>$10^3$ Hz</td>
</tr>
<tr>
<td>Scalar</td>
<td>$1 - 100$ Hz</td>
</tr>
<tr>
<td>Dipolar</td>
<td>$10^3$ Hz</td>
</tr>
<tr>
<td>Quadrupolar</td>
<td>$10^6$ Hz</td>
</tr>
</tbody>
</table>

Together these interactions form the “internal” Hamiltonian

$$\hat{H}_{int} = \hat{H}_{cs} + \hat{H}_J + \hat{H}_d + \hat{H}_Q.$$
Chemical shift:

\[ \hat{\mathcal{H}}_{cs} = \gamma (\hat{I}_x \sigma_{xx} + \hat{I}_y \sigma_{yy} + \hat{I}_z \sigma_{zz}) B_0 \]

in the **principal axis** frame of reference (PAS), a frame of reference defined relative to the chemical shift tensor components.
Spherical tensor notation:

\[ \hat{\mathcal{H}} = \sum_{l} \sum_{m=-l}^{l} (-1)^m A_{l,m}^{(\mu)} T_{l,-m}^{(\mu)} \]

where \( \mu \) represents the type of interaction involved (e.g. dipolar, quadrupolar,...), \( l \) is the angular momentum quantum number or rank of the tensor, \( m \) is the magnetic quantum number, \( A_{l,m}^{(\mu)} \) are spatial tensor components, and \( T_{l,-m}^{(\mu)} \) are the irreducible spin tensor operators.
For the CSA interaction, the tensor components are defined as follows - Spin part:

\[ T_{20} = \frac{1}{\sqrt{6}} 2I_z B_0 \]

\[ T_{2\pm 1} = \pm \frac{1}{2} I^\pm B_0 \]

\[ T_{2\pm 2} = 0 \]

Spatial part in PAS:

\[ A_{20}^{PAS} = \sqrt{\frac{3}{2}} \gamma (\sigma_{zz} - \sigma_{iso}) \]

\[ A_{2\pm 1}^{PAS} = 0 \]

\[ A_{2\pm 2}^{PAS} = -\frac{1}{2} \gamma (\sigma_{zz} - \sigma_{iso}) \eta \]
where

\[
\sigma_{iso} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3}
\]

\[
\eta = \frac{\sigma_{yy} - \sigma_{xx}}{\sigma_{zz} - \sigma_{iso}}.
\]
To obtain the spatial part in any arbitrary frame, we need to transform or rotate to a different coordinate system. The rotations in three-dimensional space are represented by the Euler angles \((\alpha, \beta, \gamma)\), and are denoted \(R(\alpha, \beta, \gamma)\):
So to go from the PAS to the LAB frame, we use $R(\alpha, \beta, \gamma)$ and to do the reverse rotation, i.e. from LAB $\rightarrow$ PAS, we use the notation $R(\phi, \Theta, \chi)$.

\[
R(\alpha, \beta, \gamma) = R_z(\alpha)R_y(\beta)R_z(\gamma).
\]
Transforming the spatial tensors from \( \text{PAS} \rightarrow \text{LAB} \), we get

\[
A_{20}^{\text{LAB}} = \sqrt{\frac{3}{8}} \gamma (\sigma_{zz} - \sigma_{iso}) \left[ (3 \cos^2 \beta - 1) - \eta \sin^2 \beta \cos 2\alpha \right]
\]

\[
A_{2\pm1}^{\text{LAB}} = \pm \frac{1}{2} \gamma (\sigma_{zz} - \sigma_{iso}) \left[ (3 + \eta \cos 2\alpha) \cos \beta \mp i \eta \sin 2\alpha \right]
\]

\[
\times \sin \beta e^{\mp i \gamma}
\]

\[
A_{2\pm2}^{\text{LAB}} = \frac{1}{2} \gamma (\sigma_{zz} - \sigma_{iso}) e^{\mp 2i \gamma}
\]

\[
\times \left[ \frac{3}{2} \sin^2 \beta - \frac{\eta}{2} (1 + \cos^2 \beta) \cos 2\alpha \pm i \eta \cos \beta \sin 2\alpha \right]
\]
Dipolar interaction:

\[ \hat{\mathcal{H}}_D = \frac{\mu_0 \gamma_1 \gamma_2 \hbar^2}{16\pi^3} \left[ (\hat{I}_1 \cdot \hat{I}_2) r^{-3} - 3(\hat{I}_1 \cdot \vec{r})(\hat{I}_2 \cdot \vec{r}) r^{-5} \right]. \]
\[ \hat{\mathcal{H}}_D = \frac{\mu_0 \gamma_1 \gamma_2 \hbar^2}{16\pi^3 r^3} \{ A + B + C + D + E + F \} \]

where

\[ A = \hat{I}_{1z} \hat{I}_{2z} (1 - 3 \cos^2 \theta) \]

\[ B = -\frac{1}{4} \left[ \hat{I}_1^+ \hat{I}_2^- + \hat{I}_1^- \hat{I}_2^+ \right] (1 - 3 \cos^2 \theta) \]

\[ C = -\frac{3}{2} \left[ \hat{I}_1^+ \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_2^+ \right] \sin \theta \cos \theta e^{-i \phi} \]

\[ D = -\frac{3}{2} \left[ \hat{I}_1^- \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_2^- \right] \sin \theta \cos \theta e^{i \phi} \]

\[ E = -\frac{3}{4} \hat{I}_1^+ \hat{I}_2^+ \sin^2 \theta e^{-2i \phi} \]

\[ F = -\frac{3}{4} \hat{I}_1^- \hat{I}_2^- \sin^2 \theta e^{2i \phi} \]
Thus the Hamiltonian in the case of homonuclear coupling (between like spins) is

$$\hat{H}_D = \frac{-\mu_0 \gamma_1 \gamma_2 \hbar^2}{16\pi^3 r^3} \frac{1}{2} (3\cos^2 \theta - 1)[3\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_1 \cdot \hat{I}_2]$$

(8.13)

whereas in the case of heteronuclear coupling, it is given by

$$\hat{H}_D = \frac{-\mu_0 \gamma_1 \gamma_2 \hbar^2}{16\pi^3 r^3} (3\cos^2 \theta - 1)\hat{I}_{1z}\hat{I}_{2z}.$$  

(8.14)
Magic Angle Sample Spinning
How averaging of CSA works under MAS:

\[
\hat{\mathcal{H}}_{cs} = -\gamma I_z B_z + \gamma A_{00} T_{00} + \gamma A_{20}(t) T_{20}
\]

where

\[
B_z = \sigma_{zz} B_0
\]

\[
T_{00} = -\frac{1}{\sqrt{3}} I_z B_z
\]

\[
T_{20} = \sqrt{\frac{2}{3}} I_z B_z
\]
and $A_{20}$ is time-dependent due to the sample rotation. This means that the precession frequency is

$$\omega(t) = \omega_0 \left(1 - \frac{1}{\sqrt{3}} A_{00} - \sqrt{\frac{2}{3}} A_{20}(t)\right)$$

with

$$\omega_0 = -\gamma B_z.$$
In the PAS, the spatial components for the rank two tensors are given by

\[ A_{20} = \sqrt{\frac{3}{2}} \delta \]

\[ A_{2\pm 1} = 0 \]

\[ A_{2\pm 2} = \frac{1}{2} \delta \eta \]

with \( \delta = \sigma_{zz} - \sigma_{iso} \) and \( \eta = \frac{\sigma_{yy} - \sigma_{xx}}{\sigma_{zz} - \sigma_{iso}} \) and the isotropic part of the chemical shift is given by the \( A_{00} \) term, i.e.

\[ A_{00} = -\sqrt{3} \delta_{iso}. \]
Thus

\[ \omega(t) = \omega_0 \left( 1 + \delta_{iso} - \sqrt{\frac{2}{3}} A_{20}(t) \right) \]

or

\[ \omega(t) = \omega_0 \left( 1 + \delta_{iso} - \Delta \bar{\delta} - \delta(t) \right) \]

with

\[ \Delta \bar{\delta} = \sqrt{\frac{2}{3}} A_{20}(t) \]

\[ \delta(t) = \sqrt{\frac{2}{3}} A_{20}(t) - \sqrt{\frac{2}{3}} A_{20}(t) \]
In the LAB frame:

\[
\Delta \bar{\delta} = \frac{1}{2} \delta (3\cos^2 \theta - 1) \\
\ast \left[ \frac{1}{2} (3\cos^2 \beta - 1) - \frac{1}{2} \eta \sin^2 \beta \cos 2\alpha \right]
\]

\[
\delta(t) = C_1 \cos(\gamma + \omega_r t) + S_1 \sin(\gamma + \omega_r t) \\
+ C_2 \cos(2\gamma + 2\omega_r t) + S_2 \sin(2\gamma + 2\omega_r t)
\]
with

\[ C_1 = -\frac{1}{4} \delta \sin 2\theta \sin 2\beta (3 + \eta \cos 2\alpha) \]

\[ S_1 = \frac{1}{2} \delta \eta \sin 2\theta \sin \beta \sin 2\alpha \]

\[ C_2 = \sin^2 \theta \delta \left( \frac{3}{4} \sin^2 \beta - \frac{1}{4} \eta (1 + \cos^2 \beta) \cos 2\alpha \right) \]

\[ S_2 = \frac{1}{2} \delta \eta \sin^2 \theta \cos \beta \sin 2\alpha \]
Thus for $\theta = \theta_m$, one gets

\[ \Delta \bar{\delta} = 0 \]

\[ C_1 = -\frac{1}{\sqrt{2}} \delta \sin 2\beta (1 + \frac{1}{3} \eta \cos 2\alpha) \]

\[ S_1 = \frac{\sqrt{2}}{3} \delta \eta \sin \beta \sin 2\alpha \]

\[ C_2 = \frac{1}{2} \delta (\sin^2 \beta - \frac{1}{3} \eta (1 + \cos^2 \beta) \cos 2\alpha) \]

\[ S_2 = \frac{1}{3} \delta \eta \cos \beta \sin 2\alpha \]
Or rewritten in a different way:

\[
\Delta \bar{\delta} = 0
\]

\[
\delta(t) = \sum_i g_i(\alpha, \beta, \delta, \eta) \ast h_i(\gamma, \omega_r t)
\]

signal at isotropic chemical shift, with sidebands due to the term \(\omega_r t\).
e.g. $^{13}$C spectrum of alanine
1) For homonuclear spin systems:
- MAS suppresses the CSA interactions
- (multiple-pulse) decoupling suppresses the homonuclear dipolar interaction (e.g. Lee-Goldburg decoupling, Frequency-switched Lee-Goldburg decoupling, WAHUHA)

2) For heteronuclear spin systems:
- MAS suppresses the CSA interactions
- decoupling suppresses the heteronuclear dipolar interaction (e.g. cw, TPPM)
<table>
<thead>
<tr>
<th>Sample</th>
<th>MAS</th>
<th>Static</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>Isotropic CS</td>
<td>CSA</td>
</tr>
<tr>
<td></td>
<td>Isotropic J</td>
<td>Isotropic J</td>
</tr>
<tr>
<td></td>
<td>Part. averaged D</td>
<td>Pake pattern</td>
</tr>
<tr>
<td>Oriented Sample</td>
<td>Isotropic CS</td>
<td>CS=f(α,β)</td>
</tr>
<tr>
<td></td>
<td>Isotropic J</td>
<td>Isotropic J</td>
</tr>
<tr>
<td></td>
<td>Part. averaged D</td>
<td>D=g(α,β)</td>
</tr>
</tbody>
</table>

where CS=chemical shift, J=scalar interaction, and D=dipolar interaction, and where α and β define the orientation of the interaction tensor or vector with respect to the external magnetic field $\vec{B}_0$. 
Alternative methods: Magic angle hopping and Magic angle turning

MAS $\rightarrow$ continuous rotation, averaging over a full rotation

**Magic Angle Hopping**

It is also possible to average $\delta(t)$ to zero by using a set of discrete values. These are

$$\delta(0) + \delta\left(\frac{2\pi}{3\omega_r}\right) + \delta\left(\frac{4\pi}{3\omega_r}\right)$$

i.e. three orientations that are different by 120 degrees.
Given

\[ \delta(t) = C_1 \cos(\gamma + \omega_r t) + S_1 \sin(\gamma + \omega_r t) \]
\[ + C_2 \cos(2\gamma + 2\omega_r t) + S_2 \sin(2\gamma + 2\omega_r t) \]

with

\[ C_1 = -\frac{1}{4} \delta \sin 2\theta \sin 2\beta (3 + \eta \cos 2\alpha) \]
\[ S_1 = \frac{1}{2} \eta \sin 2\theta \sin \beta \sin 2\alpha \]
\[ C_2 = \sin^2 \theta \delta \left( \frac{3}{4} \sin^2 \beta - \frac{1}{4} \eta \right) (1 + \cos^2 \beta) \cos 2\alpha \]
\[ S_2 = \frac{1}{2} \eta \sin^2 \theta \cos \beta \sin 2\alpha \]
\[
\begin{align*}
\delta(0) &= C_1 \cos(\gamma) + S_1 \sin(\gamma) \\
&\quad + C_2 \cos(2\gamma) + S_2 \sin(2\gamma) \\
\delta\left(\frac{2\pi}{3\omega_r}\right) &= -\frac{1}{2}C_1 \cos(\gamma) - C_1 \sin(\gamma) \sin(120) \\
&\quad - \frac{1}{2}S_1 \sin(\gamma) + S_1 \cos(\gamma) \sin(120) \\
&\quad - \frac{1}{2}C_2 \cos(2\gamma) + C_2 \sin(2\gamma) \sin(120) \\
&\quad - \frac{1}{2}S_2 \sin(2\gamma) - S_2 \cos(2\gamma) \sin(120)
\end{align*}
\]
\[ \delta \left( \frac{4\pi}{3\omega_r} \right) = -\frac{1}{2} C_1 \cos(\gamma) + C_1 \sin(\gamma) \sin(120) \]

\[ -\frac{1}{2} S_1 \sin(\gamma) - S_1 \cos(\gamma) \sin(120) \]

\[ -\frac{1}{2} C_2 \cos(2\gamma) - C_2 \sin(2\gamma) \sin(120) \]

\[ -\frac{1}{2} S_2 \sin(2\gamma) + S_2 \cos(2\gamma) \sin(120) \]
Final result:

\[ \delta(0) + \delta\left(\frac{2\pi}{3\omega_r}\right) + \delta\left(\frac{4\pi}{3\omega_r}\right) = 0 \]

How is this achieved experimentally?
Fig. 2. (A) Picture of the DMAT apparatus showing: (a) the NMR probe; (b) the DC Servo motor; and (c) the computer programmable control box. (B) Close-up picture of the NMR probe with various parts labeled: (1) the teetiled pulley assembly (i.e., the DMAT sample rotation module) that fits into the sample rotor; (2) the first teetiled driving belt; (3) the two pulleys with flat surfaces that are rotating in opposing directions, which are used to change the directions of rotation of the belt (2); (4) a teetiled pulley that is identical to (1); and (5) a teetiled pulley that is integrated with (4) such that a full rotation of (5) causes a full rotation of (4). (5) is then connected to the input pulley of the NMR probe as shown in (A). (C) The drawing containing only the nulling assembly in (B) for changing the direction of
Analogous approach: magic angle turning

- rotor is synchronized so that signal is detected at the appropriate angles (120° apart)
- requires slow spinning

Figure 1. Pulse sequence of the chemical shift and CSA correlation experiment using slow magic angle spinning. The last segment of the evolution period is incorporated into the acquisition period, and all of the narrow pulses are 90° pulses.
A quick look at MAS and quadrupolar nuclei:

\[
< \nu_Q >_{rot} = A_0 + A_2 P_2(\cos \beta) + A_4 P_4(\cos \beta)
\]

\[
P_2(\cos \theta) = (3 \cos^2 \theta - 1)
\]

\[
P_4(\cos \theta) = (35 \cos^4 \theta - 30 \cos^2 \theta + 3)
\]

where \( A_0 \) is the isotropic shift, and \( A_2 \) and \( A_4 \) are functions of \( \omega_Q, \omega_0, \eta \) and the relative orientation of the quadrupolar tensor and rotor axis. \( \beta \) is the angle between the rotor axis and the static magnetic field \( \vec{B}_0 \).
$P_2(cos\beta)$ and $P_4(cos\beta)$ are averaged to zero and $-7/18$, respectively, for sample rotation at the magic angle. Hence MAS only reduces the linewidths of the resonances obtained from powdered samples by approximately $1/3$, and for large $\chi$ significant second-order quadrupolar line broadening remains.
To average the P4 term completely $\rightarrow$ dynamic angle spinning (DAS) or double rotation (DOR)
B) Cross-polarization

Why use it? To enhance sensitivity (analogous to INEPT in solution state)

\[
\frac{S}{N} = \frac{k_{e f f, x} N_x \gamma_x 5/2 h^2 B_0 T_{2, x}}{4(2\pi)^2 kT}
\]

or

\[
\frac{S}{N} = k_{e f f, x} \sqrt{\omega_s} M_S^{90} T_{2, s}.
\]

with the magnetization measured after a 90 degree pulse being:

\[
M_S^{90} = \frac{N_S \gamma_S^2 h^2 B_0}{4(2\pi)^2 kT}.
\]
If one used Hartmann-Hahn cross-polarization (HHCP) instead, i.e. the pulse sequence shown below with

\[ B_{1I} \gamma_I = B_{1S} \gamma_S \]
then the magnetization measured is given by

\[ M_{S}^{HHCP} = \frac{1}{2} \frac{\gamma_I}{\gamma_S} \sqrt{\frac{N_I}{N_S}} M_{S}^{90}. \]

Therefore the enhancement in signal to noise that one can expect from using HHCP is

\[ \left( \frac{S}{N} \right)^{HHCP} \left( \frac{S}{N} \right)^{90} = \frac{1}{2} \frac{\gamma_I}{\gamma_S}. \]

Thus for \( I=^1H \) and \( S=^{13}C \), the expected enhancement is

\[ \left( \frac{S}{N} \right)^{HHCP} \left( \frac{S}{N} \right)^{90} = \frac{1}{2} \frac{\gamma_H}{\gamma_C} = 2. \]
One can also use the analogy from thermodynamics (though not fully correct) of the equilibration of a hot and cold bath when they come into contact, i.e.

oscillations $\rightarrow$ proportional to dipolar coupling constant
In this case, the enhancement that one would expect is given by

\[ M_{S}^{\text{adiabaticCP}} = \frac{\gamma I}{\gamma S} \sqrt{\frac{N_I}{N_S}} M_{S}^{90}. \]

Therefore the enhancement in signal to noise that one can expect from using adiabaticCP is

\[ \left( \frac{S}{N} \right)^{\text{adiabaticCP}} = \frac{\gamma I}{\gamma S} \left( \frac{S}{N} \right)^{90}. \]
Thus for $I = ^1 H$ and $S = ^{13} C$, the expected enhancement is

\[
\frac{\left(\frac{S}{N}\right)^{adiabatic\, CP}}{\left(\frac{S}{N}\right)^{90}} = \frac{\gamma_H}{\gamma_C} = 4
\]

and for $I = ^1 H$ and $S = ^{15} N$, the expected enhancement is

\[
\frac{\left(\frac{S}{N}\right)^{adiabatic\, CP}}{\left(\frac{S}{N}\right)^{90}} = \frac{\gamma_H}{\gamma_N} = 10.
\]
Adiabatic transfer is achieved experimentally by either using a ramp (RAMP-CP) or a tangent (APHH-CP):

\[ \omega_{II} = \omega_{1s} \]
\[ \omega_{II} = \omega_{1s} \]
References:

For RAMP-CP


For APHH-CP


Figure 5  CP-matching curves for various spinning rates for a solid with relatively weak dipolar couplings, e.g. hexamethylbenzene
\[ B_{1S} \gamma_S - B_{1I} \gamma_I = n \omega_r \]

or

\[ \omega_{1S} - \omega_{1I} = n \omega_r \]

with \( n = 0, \pm 1, \pm 2, \ldots \) and \( \omega_r \) is the (angular) spinning frequency.

This means that the match condition is separated into sidebands, separated by the spinning speed, i.e.
Figure 5  CP-matching curves for various spinning rates for a solid with relatively weak dipolar couplings, e.g. hexamethylbenzene
AMCP
References:
FIG. 6. CP/MAS matching spectra of the $^{13}$CH$_3$ carbon resonance line in adamantane and corresponding simulation for (a) standard HHCP, (b) a rotor-synchronized cosine modulation of amplitude 2.1 $\omega_r$ performed on the carbon rf field, (c)–(d) the pulse sequences of Fig. 4(a) and 4(b), respectively. For all experiments, the MAS frequency was set to 5 kHz, the mixing time to 1.2 ms, and the proton rf field strength, $\omega_{1f}^{(0)}$, to 23.8 kHz. The CP matching spectra are plotted on the same amplitude scale and can be directly
CP for Spectral Editing

\[ ^1H \rightarrow ^{13}C \text{ CP} \]

\[ C_{\text{CP}} = 100 \mu s \rightarrow 5 \text{ ms} \]

\[ C_{\text{CP}} = 100 \mu s \rightarrow 20 \text{ ms} \]
Figure 3 Subspectra constructed from the data in Figure 2. (a) Normal CP MAS spectrum again for comparison. (b) \text{CH}_0\text{-only}. (c) \text{CH}_1\text{-only}. (d) \text{CH}_2\text{-only}. (e) \text{CH}_3\text{-only}. Some of the assignments made possible by the editing technique are given in the inset.
Figure 1  Sequences used in the editing protocol of Wu et al. All employ simultaneous phase inversion to alleviate problems with Hartmann–Hahn mismatches. (a) CP sequence. The additional spin locking delay $\tau_{SL}$ is used to make the total $^{13}$C spin locking time the same in all of the sequences. (b) SCPPPI sequence used to acquire CH$_2$-only spectra. (c) Depolarization sequence. The time $\tau_{SL}$ is added in these sequences mainly to minimize distortions from $^1$H rotating frame relaxation.
FIG. 4. Pulse sequence diagrams for the experimental procedures used to effect transfer of magnetization between $^1$H and $^{15}$N nuclei. The letters correspond to the plots in Fig. 5. A. Conventional cross-polarization (CP). B. CP with Lee–Goldburg irradiation. C. Polarization-inversion of the $^1$H magnetization following the CP sequence. D. CP with WIM-24 irradiation. E. CP with SEMA. F. PIEMA.

FIG. 5. Plots of the amplitude corresponding to magnetization as a function of the length of the transfer interval. The letters correspond to the pulse sequences in Fig. 4.