Supporting Information

**Homonuclear Decoupling in $^1$H NMR of Solids by Remote Correlation**

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anie_201916335_sm_miscellaneous_information.pdf
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**All raw data can be accessed at the following DOI:**
https://doi.org/10.5281/zenodo.3712757
Experimental details

Solid-state NMR experiments were performed at room temperature on an 18.8 T Bruker Avance Neo spectrometer equipped with a 0.7 mm triple resonance HCN CP-MAS probe. Data were acquired on three different samples. The powdered samples of thymol (2-Isopropyl-5-methylphenol), β-AspAla ((2S)-2-amino-3-{{[(1S)-1-carboxyethyl]carbamoylpropanoic acid}, and strychnine were purchased from AppliChem, Bachem, and Signal-Aldrich respectively and were used without further recrystallization, after mild crushing with a mortar and a pestle.

All data were acquired with rotor synchronized delays, at a sample spinning speed of 100 kHz. Presaturation was applied on the $^1$H channel. For the thymol and β-AspAla spectra, a proton pulse with amplitude $\nu_1$=294 kHz was used, whereas for the strychnine data a $\nu_1$=278 kHz was used.

All 2D spectra were acquired with the States-TPPI acquisition method. For the 2D ZQF COSY and z-COSY experiments a total of 256 $t_1$ points were acquired with $t_2$ acquisition times of 10.2 ms and with a maximum $t_1$ delay of 12.8 ms. The recycle delay was 5 s and for each $t_1$ increment 8 and 32 scans were acquired respectively. All anti-z-COSY spectra of thymol were acquired with 256 $t_1$ increments and a maximum $t_1$ delay of 10.2 ms, whereas the anti-z-COSY spectra of β-AspAla were acquired with 448 $t_1$ increments and a maximum $t_1$ delay of 20.1 ms. For thymol, the $t_2$ acquisition time was 10.2 ms and for β-AspAla 12.8 ms. When flip angles of 90°, 45°, 20°, 15° were used, 8 scans were acquired, while for flip angles of 8°, 5°, and 3°, 16, 32 and 64 scans were acquired respectively. The 2D anti-z-COSY experiment of strychnine was acquired with 180 $t_1$ points, a maximum $t_1$ delay of 8.1 ms and a $t_2$ acquisition time of 8 ms. The flip angle was set to 8°, 32 scans were acquired for each $t_1$ point, and the recycle delay was 50 s.

The 1D echo spectra of thymol and β-AspAla were acquired with 5 s recycle time, and 10 ms acquisition time. The spectrum of strychnine was acquired with 50 s recycle time, and 8 ms acquisition time.

All processing was done either using the Bruker software TopSpin 4.0.6, or with homemade MATLAB scripts. All 2D anti-z-COSY spectra were double Fourier transformed, and sheared twice, once parallel to $F_1$ with a shear factor of $\kappa_1=-1$ and once more parallel to the new $F'_2$ dimension with a new shear factor of $\kappa_1=+(1/2)$, where the shear factor $\kappa_1$ is related to the shear angle $\theta$ according to the equation $\tan\theta = \kappa_1$. This was done at TopSpin using the ajp_share “au” program. After double shearing, an integral projection onto $F_2$ of the $F_1$ range spanned by the lineshape of the signals was taken.

$^1$H chemical shifts were reference according to literature.

The experimental details are summarized in the following tables:
Thymol:

| Experiment | $\omega / 2\pi$ (kHz) | $\omega R / 2\pi$ (kHz) | Total exp. time | $t_2$ acquisition time / ms | Maximum $t_1$ increment / ms | $t_{d2}$ complex points | $t_{d1}$ complex points | NS | $d_1$ /s | $\tau_z$ / μs |
|------------|----------------------|----------------------|-----------------|--------------------------|--------------------------|-----------------------|-----------------------|----|-------|-------------|
| echo detected | 100 | 312.5 | 20 s | 10.2 ms | - | 2048 | - | 4 | 5 | 10 |
| ZQF-COSY | 100 | 294 | | 10.2 ms | 12.8 | 2048 | 128 | 8 | 5 | 10 |
| z-COSY (5°) | 100 | 294 | 2 h 52 min | 10.2 ms | 12.8 | 2048 | 128 | 32 | 5 | 10 |
| anti-z-COSY (90°) | 100 | 294 | 2 h 52 min | 10.2 ms | 12.8 | 2048 | 128 | 8 | 5 | 10 |
| anti-z-COSY (45°) | 100 | 294 | 2 h 52 min | 10.2 ms | 12.8 | 2048 | 128 | 8 | 5 | 10 |
| anti-z-COSY (20°) | 100 | 294 | 2 h 52 min | 10.2 ms | 12.8 | 2048 | 128 | 8 | 5 | 10 |
| anti-z-COSY (15°) | 100 | 294 | 2 h 52 min | 10.2 ms | 12.8 | 2048 | 128 | 8 | 5 | 10 |
| anti-z-COSY (10°) | 100 | 294 | 5 h 45 min | 10.2 ms | 12.8 | 2048 | 128 | 16 | 5 | 10 |
| anti-z-COSY (8°) | 100 | 294 | 11 h 31 min | 10.2 ms | 12.8 | 2048 | 128 | 32 | 5 | 10 |
| anti-z-COSY (5°) | 100 | 294 | 23 h 2 min | 10.2 ms | 12.8 | 2048 | 128 | 64 | 5 | 10 |
| anti-z-COSY (3°) | 100 | 294 | | | | | |

Table S1: Experimental details of experiments acquired on a powdered sample of thymol.

β-AspAla:

| Experiment | $\omega / 2\pi$ (kHz) | $\omega R / 2\pi$ (kHz) | Total exp. time | $t_2$ acquisition time / ms | Maximum $t_1$ increment / ms | $t_{d2}$ complex points | $t_{d1}$ complex points | NS | $d_1$ /s | $\tau_z$ / μs |
|------------|----------------------|----------------------|-----------------|--------------------------|--------------------------|-----------------------|-----------------------|----|-------|-------------|
| echo detected | 100 | 294 | 20 s | 10 | - | 2048 | - | 4 | 5 | 10 |
| anti-z-COSY (90°) | 100 | 294 | 5 h 2 min | 12.8 | 20.1 | 2560 | 224 | 8 | 5 | 10 |
| anti-z-COSY (45°) | 100 | 294 | 5 h 2 min | 12.8 | 20.1 | 2560 | 224 | 8 | 5 | 10 |
| anti-z-COSY (20°) | 100 | 294 | 5 h 2 min | 12.8 | 20.1 | 2560 | 224 | 8 | 5 | 10 |
| anti-z-COSY (15°) | 100 | 294 | 5 h 2 min | 12.8 | 20.1 | 2560 | 224 | 8 | 5 | 10 |
| anti-z-COSY (10°) | 100 | 294 | 5 h 2 min | 12.8 | 20.1 | 2560 | 224 | 8 | 5 | 10 |
| anti-z-COSY (8°) | 100 | 294 | 10 h 5 min | 12.8 | 20.1 | 2560 | 224 | 16 | 5 | 10 |
| anti-z-COSY (5°) | 100 | 294 | 10 h 5 min | 12.8 | 20.1 | 2560 | 224 | 16 | 5 | 10 |
| anti-z-COSY (3°) | 100 | 294 | 20 h 11 min | 12.8 | 20.1 | 2560 | 224 | 32 | 5 | 10 |

Table S2: Experimental details of experiments acquired on a powdered sample of β-AspAla.
Strychnine:

| Experiment | (ω₁/2π) /kHz | (ω₂/2π) /kHz | Total exp. time | t₂ acquisition time / ms | Maximum t₁ increment / ms | td₂ complex points | td₁ complex points | NS | d₁ /s | τᵣ / μs |
|------------|---------------|---------------|----------------|--------------------------|----------------------------|---------------------|---------------------|----|------|--------|
| echo       | 100           | 277.8         | 3 min 20 s     | 8                        | -                          | 1600                | -                   | 4  | 50   | 10     |
| detected   | 100           | 277.8         | 3d 8 h 12 min  | 8                        | 8                          | 1600                | 90                  | 32 | 50   | 10     |
| anti-z-COSY (8°) | 100           | 277.8         | 3d 8 h 12 min  | 8                        | 8                          | 1600                | 90                  | 32 | 50   | 10     |

Table S3: Experimental details of experiments acquired on a powdered sample of strychnine.

Processing of experimental data

1) All 2D anti-z-COSY spectra were double Fourier transformed, zero filled to 8k and 1k points in F₂ and F₁ respectively, and then sheared twice, once parallel to F₁ and once more parallel to the new F´₂ dimension using the ajp_share "au" program written by A. J. Pell.[1]

2) An integral projection onto F₂ of the F₁ range spanned by the lineshape of the signals was taken in order to avoid the addition of unnecessary noise in the extracted 1D spectrum. For thymol, H4 was chosen was a reference point, and for β-AspAla H7.

3) Peak widths at half height were measured using the peakw command in tospin 4.0.6.
Thymol spectra acquired with different flip angles

Figure S1: Spectra of thymol obtained as integral projections from 45° sheared 2D anti-z-COSY spectra acquired with flip angles, $\beta$, of 90°, 45°, 20°, 15°, 10°, 8°, 5°, and 3° at 100 kHz MAS. The top spectrum shows the result of the echo-detected experiment at the same spin rate.

Linewidths at half height of thymol spectra

| Proton/\(\beta\) | echo | 90  | 45  | 20  | 15  | 10  | 8   | 5   | 3   |
|------------------|------|-----|-----|-----|-----|-----|-----|-----|-----|
| H1               | 418  | 359 | 336 | 294 | 279 | 249 | 252 | 232 | 208 |
| H2               | 386  | 336 | 304 | 269 | 262 | 246 | 233 | 229 | 194 |
| H3               | 394  | 350 | 325 | 291 | 283 | 255 | 238 | 234 | 245 |
| H4               | 388  | 346 | 323 | 294 | 275 | 256 | 256 | 239 | 218 |
| H5\(\ast\)      | 752  | 649 | 627 | 564 | 533 | 524 | 521 | 516 | 501 |
| H5\(\ast\ast\)   | 752  | 649 | 627 | 564 | 533 | 524 | 521 | 516 | 501 |
| H6               | 443  | 433 | 395 | 301 | 283 | 249 | 251 | 236 | 221 |

Table S4: Linewidths of thymol spectra measured at half height.

The asterisks denote protons which are represented by peaks that overlap.
**T₂’ measurements on thymol**

| Proton | Echo (measured linewidths in Hz) | T₂’ (ms) | Δ (1/(π T₂’) in Hz) |
|--------|----------------------------------|----------|---------------------|
| H1     | 417                              | 2.71     | 121                 |
| H2     | 393                              | 3.59     | 89                  |
| H3     | 409                              | 2.64     | 118                 |
| H4     | 391                              | 2.79     | 114                 |

Table S5: T₂ relaxation measurements on a sample of thymol.

Linewidths at half height of echo-detected spectra acquired on the same day and at the same MAS rate were measured.

**2D contour plots of anti-z-COSY spectra**

Figure S2: a) and b) anti-z-COSY spectra of thymol acquired with flip angles of 90° and 5° respectively. c) and d) anti-z-COSY spectra of β-AspAla acquired with flip angles of 90° and 5° respectively. The contour levels are plotted in a way that the peaks of H4 of thymol and H7 of β-AspAla have the same intensity in the 90° and 5° anti-z-COSY spectra.
Linewidths at half height of $\beta$-AspAla spectra

| Proton/\(\beta^*\) | Echo (measured linewidths in Hz) | T2' (ms) | \(\Delta (1/\pi T2')\) in Hz |
|---------------------|----------------------------------|----------|------------------------------|
| H8                  | 227                              | 5.41     | 59                           |
| H5                  | 322                              | 3.71     | 86                           |
| H4                  | 342                              | 2.5      | 127                          |
| H7                  | 219                              | 4.97     | 64                           |
| H3                  | 267                              | 3.07     | 104                          |
| H1                  | 301                              | 2.82     | 113                          |
| H2                  | 303                              | 2.92     | 109                          |
| H6                  | 264                              | 3.2      | 100                          |

Table S6: Linewidths of $\beta$-AspAla spectra measured at half height.

**T2’ measurements on $\beta$-AspAla**

| Proton | Echo (measured linewidths in Hz) | T2' (ms) | \(\Delta (1/\pi T2')\) in Hz |
|--------|----------------------------------|----------|------------------------------|
| H8     | 227                              | 5.41     | 59                           |
| H5     | 322                              | 3.71     | 86                           |
| H4     | 342                              | 2.5      | 127                          |
| H7     | 219                              | 4.97     | 64                           |
| H3     | 267                              | 3.07     | 104                          |
| H1     | 301                              | 2.82     | 113                          |
| H2     | 303                              | 2.92     | 109                          |
| H6     | 264                              | 3.2      | 100                          |

Table S7: T2 relaxation measurements on a sample of $\beta$-AspAla.

Linewidths at half height of echo-detected MAS spectra acquired on the same day and at the same MAS rate were measured.

**SPINACH simulations – single crystal**

Spectra were simulated using SPINACH\(^3\) which runs inside the MATLAB framework, and were processed on Topspin 4.0.6 similarly to the experimental data. The transfer of the data from MATLAB to Topspin was done using a homemade script written by M. Foroozandeh.

1) **Spin systems in figure 2:**

For the 3 spins simulations, the three chemical shifts were all different and isotropic, and all spins were dipolar coupled. No scalar couplings were included in the spin system. All simulations were performed invoking magic angle sample spinning, and using a single crystal with a single orientation in figure 2b, and two different orientations with the same weight in Figure 2c-f. A Gaussian line broadening of 8 Hz was applied in both dimensions of the 2D plots prior to Fourier transformation.
Table S8: Spin system parameters for the spin system illustrated in Fig. 2.

| Zeeman Eigenvalues (ppm) | Dipolar Coupling Eigenvalues (Hz) | Dipolar Coupling Euler Angles |
|--------------------------|----------------------------------|-------------------------------|
| Figure 2a                | Ω₁ = 9.0                          | D₁₂ = 18000 Hz                | E₁₂ = (π/5 π/7 π/20) |
|                          | Ω₂ = 15.0                         |                               |                  |
| Figure 2b                | Ω₁ = 2.5                          | D₁₂ = 3600 Hz                 | E₁₂ = π*(0.0 170 0.0)/180 |
|                          | Ω₂ = 45.0                         | D₁₂ = -24000 Hz               | E₁₂ = π*(0.0 190 0.0)/180 |
|                          | Ω₃ = 40.0                         | D₂₃ = -12500 Hz               | E₂₃ = π*(0.0 100 0.0)/180 |
| Figure 2c-f              | Ω₁ = 4.0                          | D₁₂ = 4000 Hz                 | E₁₂ = (π/6 π/2 π/20) |
|                          | Ω₂ = 3.6                          | D₁₃ = 6600 Hz                 | E₁₃ = (π/4 π/2 π/3) |
|                          | Ω₃ = 12.0                         | D₂₃ = 4400 Hz                 | E₂₃ = (π/3 π/3 π/2) |

Orientations File:

α = [0 0.3142]
β = [0 1.0472]
γ = [0 3.491]
weights = [1 1]

Simulation parameters of Figure 2e-f:

| Magnetic field | 14.0 T |
|----------------|--------|
| Spectral Width in F₁ | 10000 Hz |
| Spectral Width in F₂ | 10000 Hz |
| Number of complex points in F₁ | 4096 |
| Number of complex points in F₂ | 4096 |
| Spectral Offset | 4801.04 Hz |
| β angle | 3° |
| MAS rate | 10 kHz |

Table S9: Simulation parameters for the spin system illustrated in Fig. 2.

The Spinach input files used are given below.
**Figure S3**: A part of an ABC spin system for a single crystal with two different orientations. ZQF and anti-z-COSY ($\beta$ of 3°) simulations were performed at different MAS rates: 8, 10, 12, and 20 kHz.

**Figure S4**: a) One-dimensional $^1$H spectrum simulated with SPINACH for an ABC spin system of a single crystal with two different orientations. b) ZQF, z-COSY ($\beta$ of 3°), and anti-z-COSY ($\beta$ of 3°) simulations of the same system performed at 10 kHz MAS rate.
2) $A_2B$ Equivalent spin system:

A spin system of 2 equivalent and of an additional non-equivalent spin was used. The chemical shifts were isotropic and all spins shared dipolar couplings with one another. No scalar couplings were included in the spin system. All simulations were performed invoking magic angle sample spinning, and using a single crystal with a single orientation. A Gaussian line broadening of 8.5 Hz was applied in both dimensions of the 2D plots prior to Fourier transformation.

| Zeeman Eigenvalues (ppm) | Dipolar Coupling Eigenvalues (Hz) | Dipolar Coupling Euler Angles |
|--------------------------|----------------------------------|------------------------------|
| **Figure S5**            |                                  |                              |
| $\Omega_1 = 2.6$         | $D_{12} = 4000 \text{ Hz}$       | $E_{12} = (\pi/6 \pi/2 \pi/20)$ |
| $\Omega_2 = 4.0$         | $D_{13} = 10000 \text{ Hz}$      | $E_{13} = (\pi/4 \pi/2 \pi/3)$ |
| $\Omega_3 = 4.0$         | $D_{23} = 10000 \text{ Hz}$      | $E_{23} = (\pi/3 \pi/3 \pi/2)$ |

Table S10: Spin system parameters for the $A_2B$ spin system.

Simulation parameters:

| Magnetic field | 14.0 T |
|----------------|--------|
| Spectral Width in $F_1$ | 2500 Hz |
| Spectral Width in $F_2$ | 2500 Hz |
| Number of complex points in $F_1$ | 512 |
| Number of complex points in $F_2$ | 512 |
| Spectral Offset | 2000 Hz |
| $\beta$ angle | $3^\circ$ |
| MAS rate | 20000 |

Table S11: Simulation parameters for the $A_2B$ spin system.
Figure S5: The top part of the figure shows the 45° projections extracted from the ZQF COSY and anti-z-COSY (3°) simulations of the spin system described above. The lower part shows the diagonal peak regions of the 2D COSY spectra.

**SPINACH simulations – powder pattern of 4 and 5 spins**

A spin system of 4 or 5 inequivalent spins was used. The chemical shifts included chemical shift anisotropy, and all spins shared dipolar couplings with one another. Scalar couplings were also included (or not) in the spin system. All simulations were performed with magic angle spinning using either 42 (5 spins simulations) or 162 (4 spins simulations) orientations on an icosahedral grid. No line broadening was applied in the 2D plots.
4 spin simulations

Simulation parameters:

| Magnetic field | 14.0 T |
|---------------|--------|
| Spectral Width in $F_1$ | 10000 Hz |
| Spectral Width in $F_2$ | 10000 Hz |
| Number of complex points in $F_1$ | 256 |
| Number of complex points in $F_2$ | 256 |
| Spectral Offset | 3500 Hz |
| $\beta$ angle | 3° |
| MAS rate | 60000 |

Table S12: Simulation parameters for the 4 spins powder average.

| Zeeman Eigenvalues (ppm) | Zeeman Euler Angles | Dipolar Coupling Eigenvalues (Hz) | Dipolar Coupling Euler Angles | Scalar Coupling (Hz) |
|--------------------------|---------------------|---------------------------------|-----------------------------|---------------------|
| $\Omega_1 = (1.6 \ 2.6 \ 0.6)$ | $ZE_1 = (\pi/7 \ \pi/6 \ \pi/11)$ | $D_{12} = 32000$ | $E_{12} = \pi^* (0 \ 130 0)/180$ | $J_{12} = 10$ |
| $\Omega_2 = (6.0 \ 4.0 \ 2.0)$ | $ZE_2 = (\pi/3 \ \pi/4 \ \pi/2)$ | $D_{13} = 16600$ | $E_{13} = \pi^* (0 \ 120 0)/180$ | $J_{13} = 9$ |
| $\Omega_3 = (7.5 \ 6.5 \ 8.0)$ | $ZE_3 = (\pi/20 \ \pi/10 \ \pi/7)$ | $D_{14} = 56000$ | $E_{14} = \pi^* (0 \ 140 0)/180$ | $J_{14} = -5$ |
| $\Omega_4 = (10.0 \ 10.0 \ 10.0)$ | $ZE_4 = (\pi/4 \ \pi/2 \ \pi/9)$ | $D_{23} = 67200$ | $E_{23} = \pi^* (0 \ 150 0)/180$ | $J_{23} = 5$ |
|                           |                     | $D_{24} = 24000$ | $E_{24} = \pi^* (0 \ 160 0)/180$ | $J_{24} = 4$ |
|                           |                     | $D_{34} = 36800$ | $E_{34} = \pi^* (0 \ 135 0)/180$ | $J_{34} = 7$ |

Table S13: Spin system parameters for the 4 spin powder average.
Figure S6: 45° projections extracted from the ZQF COSY and anti-z-COSY (3°) simulations of the 4 spin system described above simulated at a 60 kHz MAS rate. In the top part of the figure J couplings are included and in the bottom part they are omitted. We note that the choice of Euler angles has a fairly strong effect on the overall lineshape and line broadening observed in the simulations for limited numbers of spins. We do not expect them to reproduce the experimental spectra quantitatively. The parameter dependencies of these simulations will be explored more extensively in future work.

5 spin simulations

Simulation parameters:

| Magnetic field | 14.0 T |
|----------------|--------|
| Spectral Width in $F_1$ | 12000 Hz |
| Spectral Width in $F_2$ | 12000 Hz |
| Number of complex points in $F_1$ | 256 |
| Number of complex points in $F_2$ | 256 |
| Spectral Offset | 3500 Hz |
| $\beta$ angle | 3° |
| MAS rate | 60000 |

Table S14: Simulation parameters for the 5 spin powder average.
Table S15: Spin system parameters for the 5 spins powder average.

| Zeeman Eigenvalues (ppm) | Zeeman Euler Angles | Dipolar Coupling Eigenvalues (Hz) | Dipolar Coupling Euler Angles | Scalar Coupling (Hz) |
|--------------------------|--------------------|----------------------------------|-------------------------------|---------------------|
| $\Omega_1 = (1.6 \ 2.6 \ 0.6)$ | $Z \mathcal{E}_1 = \left( \pi/7 \ \pi/6 \ \pi/11 \right)$ | $D_{12} = 32000$ | $E_{12} \times (0 \ 130 \ 0)/180$ | $J_{12} = 10$ |
| $\Omega_2 = (6.0 \ 4.0 \ 2.0)$ | $Z \mathcal{E}_2 = \left( \pi/3 \ \pi/4 \ \pi/2 \right)$ | $D_{13} = 16600$ | $E_{13} \times (0 \ 120 \ 0)/180$ | $J_{13} = 9$ |
| $\Omega_3 = (7.5 \ 6.5 \ 8.0)$ | $Z \mathcal{E}_3 = \left( \pi/20 \ \pi/10 \ \pi/7 \right)$ | $D_{14} = 56000$ | $E_{14} \times (0 \ 140 \ 0)/180$ | $J_{14} = -5$ |
| $\Omega_4 = (10.0 \ 10.0 \ 10.0)$ | $Z \mathcal{E}_4 = \left( \pi/4 \ \pi/2 \ \pi/9 \right)$ | $D_{15} = 48000$ | $E_{15} \times (0 \ 125 \ 0)/180$ | $J_{15} = -3$ |
| $\Omega_5 = (12.2 \ 12.1 \ 12.3)$ | $Z \mathcal{E}_5 = \left( \pi/3 \ \pi/2 \ \pi/6 \right)$ | $D_{23} = 67200$ | $E_{23} \times (0 \ 150 \ 0)/180$ | $J_{23} = 5$ |
| | | $D_{24} = 24000$ | $E_{24} \times (0 \ 160 \ 0)/180$ | $J_{24} = 4$ |
| | | $D_{25} = 14400$ | $E_{25} \times (0 \ 170 \ 0)/180$ | $J_{25} = 6$ |
| | | $D_{34} = 36800$ | $E_{34} \times (0 \ 135 \ 0)/180$ | $J_{34} = 7$ |
| | | $D_{35} = 46400$ | $E_{35} \times (0 \ 145 \ 0)/180$ | $J_{35} = 11$ |
| | | $D_{45} = 19200$ | $E_{45} \times (0 \ 150 \ 0)/180$ | $J_{45} = 2$ |

Figure S6: $45^\circ$ projections extracted from the ZQF COSY and anti-z-COSY (3°) simulations of the 5 spin system described above simulated at a 60 kHz MAS rate. We again note that the choice of Euler angles has a fairly strong effect on the overall lineshape and line broadening observed in the simulations for limited numbers of spins.
Average Hamiltonians under MAS

The effect of MAS on dipolar coupled nuclear spins has been the subject of many studies, both relating to observed lineshapes\cite{4} and to spin diffusion\cite{5}. A review is out of the scope here, but most pertinent to our work are the articles by Nakai and McDowell\cite{6} and Levitt et al.\cite{7} who both treated the case of two inequivalent dipolar coupled spins. Both papers provide expression for the lineshapes to second order that predict that MAS leads to removal of the splitting caused by the dipolar coupling, but that there will be a residual shift ($\Delta R$) in the position of the resonances, away from the isotropic values, due to higher order $I_z$ terms, and this shift will depend on both the chemical shift and coupling tensors. The higher-order shift is predicted to decrease as the spinning rate increases as $1/\omega^2_{rot}$. This is illustrated in figure 2a.

The case of three inequivalent spins has been treated by Scholz et al.,\cite{8} who presented the average Hamiltonian but who did not discuss the result in terms of spectral properties (since that article was focused on formalism and not applications). Malär et al.,\cite{4c} and Grommek et al.\cite{5f} have also presented the case of three equivalent spins. They also considered the inclusion of the effect of chemical shift differences on the lineshape invoking a weak coupling approximation.

Here, we have reproduced the average Hamiltonian to third order for an arbitrary ABC spin system. The result (obtained using the symbolic package SpinDynamica\cite{9} within Mathematica) is given below. (An example Mathematica notebook is also included.)

We see that in an ABC system both $I_z$ and two-spin $I_z I_z$ terms survive MAS at third order, and that the resulting spectrum consists of resonances for each spin that are again shifted from the isotropic value by a shift ($\Delta R$), and which are also split into a doublet of doublets. Both the shift and the residual splittings depend on all the spin system parameters. This is illustrated in Figure 2b. The higher-order shifts and splittings are predicted to decrease as the spinning speed is increased as $1/\omega^2_{rot}$. The exact functional dependence of the higher-order shifts and splittings on the spin system parameters is beyond the current scope and will be presented and explored in further work.

The effect of the anti-z COSY pulse sequence on these spectra is to remove the residual splittings, but to retain the residual shifts. This is illustrated in the SPINACH simulations shown in Figure 2d-f.
Second Order Average Hamiltonian in an AB spin system under MAS:

\[ \overline{H}^{AB} = \overline{H}^{AB}_{(1)} + \overline{H}^{AB}_{(2)} + \overline{H}^{AB}_{(3)} \]  

(1)

\[ \overline{H}^{AB}_{(1)} = \omega_1 I_{1z} + \omega_2 I_{2z} \]  

(2)

\[ \overline{H}^{AB}_{(2)} = 0 \]  

(3)

\[ \overline{H}^{AB}_{(3)} = \frac{1}{\omega_{\text{rot}}^2} C1 (I_{2z} - I_{1z}) \]  

(4)

where \( \omega_1 \) and \( \omega_2 \) are the isotropic chemical shifts of spin 1 and spin 2 and \( C1 \) is a function of \( \omega_1, \omega_2, \) and \( d_{12} \) which is the dipolar interaction between spin 1 and spin 2, \( d_{12} = -\left( \frac{\mu_0}{4\pi} \right) \frac{h y_1 y_2}{r_{12}^3} \times \frac{1}{2} (3 \cos \theta_{12}^2 - 1) \).

Second Order Average Hamiltonian in an ABC spin system under MAS:

\[ \overline{H}^{ABC} = \overline{H}^{ABC}_{(1)} + \overline{H}^{ABC}_{(2)} + \overline{H}^{ABC}_{(3)} \]  

(5)

\[ \overline{H}^{ABC}_{(1)} = \omega_1 I_{1z} + \omega_2 I_{2z} + \omega_3 I_{3z} \]  

(6)

where \( \omega_1, \omega_2, \) and \( \omega_3 \) are the isotropic chemical shifts of spins 1, 2, and 3 respectively.

\[ \overline{H}^{ABC}_{(2)} = 0 \]  

(7)

\[ \overline{H}^{ABC}_{(3)} = \frac{1}{\omega_{\text{rot}}^2} (C1 I_{1z} + C2 I_{2z} + C3 I_{3z} + C4 I_{1z} \cdot I_{2z} + C5 I_{1z} \cdot I_{3z} + C6 I_{2z} \cdot I_{3z}) \]  

(8)

where \( C1-6 \) are functions of \( \omega_1, \omega_2, \omega_3, d_{12}, d_{13}, \) and \( d_{23} \), and where \( d_{ab} \) is the dipolar coupling constant between spins a and b, \( d_{ab} = -\left( \frac{\mu_0}{4\pi} \right) \frac{h y_a y_b}{r_{ab}^3} \times \frac{1}{2} (3 \cos \theta_{ab}^2 - 1) \).

The average Hamiltonians of equations 3, 4, 7, and 8, show only the parts that are secular under the chemical-shift Hamiltonian.
**Anti-z-COSY at 62.5 kHz MAS**

**Experimental Details:**

| Experiment | \(\omega / (2\pi)/\text{kHz}\) | \(\omega / (2\pi)/\text{kHz}\) | Total exp. time | \(t_r\) acquisition time / ms | Maximum \(t_r\) increment / ms | \(t_d_2\) complex points | \(t_d_1\) complex points | NS | d1 / s | \(\tau_z\) / \(\mu\)s |
|------------|-------------------------------|-------------------------------|----------------|------------------------------|---------------------------|-------------------------|-------------------------|----|-------|----------------|
| ZQF COSY  | 62.5                          | 444                           | 2 h 29 min     | 10.2                         | 24.6                      | 2048                    | 128                     | 8  | 4.3   | 16          |
| ZQF COSY  | 62.5                          | 444                           | 9 h 58 min     | 10.2                         | 24.6                      | 2048                    | 128                     | 32 | 4.3   | 2           |
| ZQF COSY  | 62.5                          | 444                           | 9 h 58 min     | 10.2                         | 24.6                      | 2048                    | 128                     | 32 | 4.3   | 16          |
| ZQF COSY  | 62.5                          | 444                           | 9 h 58 min     | 10.2                         | 24.6                      | 2048                    | 128                     | 32 | 4.3   | 80          |

**Table S16:** Experimental parameters for experiments acquired on a sample of thymol at 62.5 kHz MAS.

**Spectra:**

**Figure S8:** Spectra of thymol at 62.5 kHz obtained as integral projections from 45° sheared anti-z-COSY spectra (\(\beta\) of 5°) acquired with different multiples of the rotor period for the z-filter delay. On the right, the linewidths of H1, H2, H3, and H4 are plotted as a function of the z-filter delay.
Anti-z-COSY spectrometer pulse sequence

All raw data can be accessed at the following DOI:
https://doi.org/10.5281/zenodo.3712757

; Anti-z-cosy experiment
; PM&FMP 2019
; Reference: Magn. Reson. Chem., 45, 296-316 (2007) and http://www-keeler.ch.cam.ac.uk/utilities/index.html
; Tested on Avance Neo

; PARAMETERS:
; p1 : power level for 90°/180° and small flip angle pulse
; p120 : power level for 1H saturation pulses
; p1 : 1H 90 degree pulse at p1
; p2 : 1H beta+180degree pulse at p1
; p3 : 1H beta pulse at p1
; p20 : 1H 90 degree saturation pulse at p20
; d0 : t1 delay
; d1 : recycle delay
; d51 : delay for Z-filter
; d50 : delay for Z-filter after subtraction of pulse duration
; cnst1 : multiplication factor for beta angle calculation
; cnst2 : beta angle (in degrees)
; cnst31 : spinning rate for rotor period calculation
; o1 : 1H offset
; l6 : number of rotor periods incremented for each t1 point
; ns=n*8

; $CLASS=Solids
; $DIM=2D
; $TYPE=homonuclear decoupling
; $SUBTYPE=anti-z-cosy
; $COMMENT=

#define delay t_rot
"t_rot=1/cnst31"
"cnst1=cnst2/90"
"p2=p1*cnst1+2*p1"
"p3=p1*cnst1"
"d50=d51-p3/2-p2/2"
"d0=0"
"in0=l6*t_rot"
"inf1=in0"

1 ze
2 10m
#ifdef sat
  3u p20:f1 ;saturate 1H channel
20 d20
  p20:f1 ph20^
Lo to 20 times l20

#define

3 p1:f1 ph1

d0 ; t1 increment

p2:f1 ph25 ; 180 + beta pulse
d50 ; z filter

4 go=2 ph31

10m mc #0 to 2 F1PH(ip1,id0)
exit ;end

ph1 = 0 0 0 0 2 2 2 2
ph20= 0 1
ph25= 0
ph26= 0 1 2 3
ph31= 0 1 3 3 2 3 0 1

Spinach Scripts

Pulse Sequence

% AntizCOSY sequence
% parameters.beta: sets the beta angle
% parameters.antiz: when 0 a ZQF or zCOSY is simulated, when 1 an antizCOSY
% is simulated
% by LE, PM, BS from EPFL

function fid=pm_antizcosy_solids(spin_system,parameters,H,R,K)

% Compose Liouvillian
L=H+1i*R+1i*K;

% Coherent evolution timestep
timestep2=1/parameters.sweep;
timestep1=1/parameters.sweep;

% Get the pulse operator
Lp=operator(spin_system,'L+','1H');
Lx=(Lp+Lp')/2;
Ly=(Lp-Lp')/2i;

Lx=kron(speye(parameters.spc_dim),Lx);
Ly=kron(speye(parameters.spc_dim),Ly);

p1= pi/2;
cnst1=parameters.beta/90;
cnst2=parameters.antiz;
p2=p1*cnst1+2*p1*cnst2;
p3=p1*cnst1;

% Apply the first pulse (States hypercomplex)
rhol_sin=step(spin_system,Lx,parameters.rho0,pi/2);
rhol_cos=step(spin_system,Ly,parameters.rho0,pi/2);
% Run the F1 evolution
rho2_sin=evolution(spin_system,L,[],rho1_sin,timestep1,parameters.npoints(1)-1,'trajectory');
rho2_cos=evolution(spin_system,L,[],rho1_cos,timestep1,parameters.npoints(1)-1,'trajectory');

% Apply the second pulse
rho4_sin=step(spin_system,Lx,rho2_sin,p2);
rho4_cos=step(spin_system,Lx,rho2_cos,p2);

% Select "0" coherence
rho4_sin=coherence(spin_system,rho4_sin,{{'1H',0}});
rho4_cos=coherence(spin_system,rho4_cos,{{'1H',0}});

% Apply the second pulse
rho5_sin=step(spin_system,Lx,rho4_sin,p3);
rho5_cos=step(spin_system,Lx,rho4_cos,p3);

% Run the F2 evolution
fid.sin=evolution(spin_system,I,parameters.coil,rho5_sin,timestep2,parameters.npoints(2)-1,'observable');
fid.cos=evolution(spin_system,I,parameters.coil,rho5_cos,timestep2,parameters.npoints(2)-1,'observable');

end

**AB Spin System (Fig. 2a)**

% 1H MAS spectrum of a single crystal
% computed using the FP formalism.
% 2 spins simulation
% Calculation time: depends on spin system. Seconds for 2 spins.
% from i.kuprov@soton.ac.uk
% by LE, PM, BS form EPFL

function mas_1H_1D_2spins_Xtal ();

% Spin system properties
sys.enable={'greedy','gpu'};
sys.isotopes={'1H','1H'};
inter.coupling.eigs=cell(2,2);
inter.coupling.euler=cell(2,2);
inter.coupling.scalar=cell(2,2);
cscal=1.0;
inter.zeeman.eigs{1}=[15.0 15.0 15.0]*cscal;
inter.zeeman.eigs{2}=[9.0 9.0 9.0]*cscal;
inter.zeeman.euler{1}=[pi/7 pi/6 pi/11];
inter.zeeman.euler{2}=[pi/3 pi/13 pi/2];
dscal=1.0;
inter.coupling.eigs{1,2}=[18.0 -9.0 -9.0]*dscal*1e3;

inter.coupling.euler{1,2}=[pi/5 pi/7 pi/20];

jscal=0.0;
inter.coupling.scalar{1,2}=10*jscal;

% Magnet field
sys.magnet=14;

% Basis set
bas.formalism='sphten-liouv';
bas.approximation='none';
bas.projections=+1;

% Algorithmic options
sys.tols.inter_cutoff=1.0;
sys.tols.prox_cutoff=100.0;
sys.disable={'trajlevel'};

% Spinach housekeeping
spin_system=create(sys,inter);
spin_system=basis(spin_system,bas);

% Experiment setup
parameters.rate=20000;
parameters.axis=[1 1 1];
parameters.max_rank=5;
parameters.sweep=20000;
parameters.npoints=32*1024;
parameters.zerofill=64*1024;
parameters.offset=7250;
parameters.spins={'1H'};
parameters.decouple={};
parameters.axis_units='Hz';
parameters.invert_axis=1;
parameters.grid='single_crystal';
parameters.rho0=state(spin_system,'L+', '1H', 'cheap');
parameters.coil=state(spin_system,'L+', '1H', 'cheap');
parameters.verbose=0;

% Simulation
fid=singlerot(spin_system,@acquire,parameters,'nmr');

% Apodization
fida=apodization(fid,'exp-1d',4);

% Fourier transform
spectruma=fftshift(fft(fida,parameters.zerofill));

% Plotting
figure(1); plot_1d(spin_system,real(spectruma),parameters);
end
ABC Spin System (Fig. 2b)

% 1H MAS spectrum of a single crystal
% computed using the FP formalism.
% 3 spin simulation
% Calculation time: Seconds for 3 spins.
% by LE, PM, BS form EPFL

function mas_1H_1D_3spins_Xtal ();

% Spin system properties
sys.enable={"greedy","gpu"};
sys.isotopes={"1H","1H","1H":[126]};

inter.coupling.eigs=cell(3,3);
inter.coupling.euler=cell(3,3);
inter.coupling.scalar=cell(3,3);

cscal=1.0;
inter.zeeman.eigs{1}=[45.0 45.0 45.0]*cscal;
inter.zeeman.eigs{2}=[40.0 40.0 40.0]*cscal;
inter.zeeman.eigs{10}=[2.5 2.5 2.5]*cscal;

inter.zeeman.euler{1}=[0 0 0];
inter.zeeman.euler{2}=[pi/7 pi/3 pi/5];
inter.zeeman.euler{10}=[pi/8 pi/6 pi/10];

dscal=0.2; dc=3.0; d=2.5;
inter.coupling.eigs{1,2}=[18.0 -9.0 -9.0]*dscal*1e3;
inter.coupling.eigs{1,3}=[-8 4 4]*dscal*1e3;
inter.coupling.eigs{2,3}=[-5 2.5 2.5]*dscal2*1e3;

inter.coupling.euler{1,2}=pi*[0.00 170 0.00]/180;
inter.coupling.euler{1,3}=pi*[0.00 190 0.00]/180;
inter.coupling.euler{2,3}=pi*[0.00 100 0.00]/180;

jscal=0.0;
inter.coupling.scalar{1,2}=10*jscal;
inter.coupling.scalar{1,3}=9*jscal;
inter.coupling.scalar{2,3}=5*jscal;

% Magnet field
sys.magnet=14;

% Basis set
bas.formalism='sphten-liouv';
bas.approximation='none';
bas.projections=+1;

% Algorithmic options
sys.tols.inter_cutoff=1.0;
sys.tols.prox_cutoff=100.0;
sys.disable={"trajlevel"};

% Spinach housekeeping
spin_system=create(sys,inter);
spin_system=basis(spin_system,bas);
% Experiment setup;
parameters.rate=20000;
parameters.axis=[1 1 1];
parameters.max_rank=8;
parameters.sweep=80000;
parameters.npoints=32*1024;
parameters.zerofill=8*1024;
parameters.offset=8000;
parameters.spins={'1H'};
parameters.decouple={};
parameters.axis_units='Hz';
parameters.invert_axis=1;
parameters.grid='single_crystal';
parameters.rho0=state(spin_system,'L+','1H','cheap');
parameters.coil=state(spin_system,'L+','1H','cheap');
parameters.verbose=0;

% Simulation
fid=singlerot(spin_system,@acquire,parameters,'nmr');

% Apodization
fida=apodization(fid,'exp-1d',4);

% Fourier transform
spectruma=fftshift(fft(fida,parameters.zerofill));

% Plotting
figure(1); plot_1d(spin_system,real(spectruma),parameters);
end

ABC Spin System (Fig. 2c)

% 1H MAS spectrum of a single crystal with two different orientations
% computed using the FP formalism.
% 3 spins simulation
% Calculation time: Seconds for 3 spins.
% by LE, PM, BS from EPFL

function mas_1H_1D_3spins_2o();

% Spin system properties
sys.enable={'greedy','gpu'};
sys.isotopes={'1H','1H','1H'};

inter.coupling.eigs=cell(3,3);
inter.coupling.euler=cell(3,3);
inter.coupling.scalar=cell(3,3);

cscal=1.0;
inter.zeeman.eigs{1}=[4.0 4.0 4.0]*cscal;
inter.zeeman.eigs{2}=[3.6 3.6 3.6]*cscal;
inter.zeeman.eigs{3}=[12 12 12]*cscal;
inter.zeeman.euler{1}=[pi/7 pi/6 pi/11];
inter.zeeman.euler{2}=[\pi/3 \pi/13 \pi/2];
inter.zeeman.euler{10}=[\pi/3 \pi/10 \pi/2];

dscal=1.0;
inter.coupling.eigs{1,2}=[4 -2 -2]*dscal*1e3;
inter.coupling.eigs{1,3}=[6.6 -3.3 -3.3]*dscal*1e3;
inter.coupling.eigs{2,3}=[4.4 -2.2 -2.2]*dscal*1e3;

inter.coupling.euler{1,2}=[\pi/6 \pi/2 \pi/20];
inter.coupling.euler{1,3}=[\pi/4 \pi/2 \pi/3];
inter.coupling.euler{2,3}=[\pi/3 \pi/3 \pi/2];

jscal=0.0;
inter.coupling.scalar{1,2}=10*jscal;
inter.coupling.scalar{1,3}=9*jscal;
inter.coupling.scalar{2,3}=5*jscal;

% Magnet field
sys.magnet=14;

% Basis set
bas.formalism='sphten-liouv';
bas.approximation='none';
bas.projections=+1;

% Algorithmic options
sys.tols.inter_cutoff=1.0;
sys.tols.prox_cutoff=100.0;
sys.disable={'trajlevel'};

% Spinach housekeeping
spin_system=create(sys,inter);
spin_system=basis(spin_system,bas);

% Experiment setup;
parameters.rate=8000;
parameters.axis=[1 1 1];
parameters.max_rank=5;
parameters.sweep=10000;
parameters.npoints=2*1024;
parameters.zerofill=4*1024;
parameters.offset=4801.04;
parameters.spins={'1H'};
parameters.decouple={};
parameters.axis_units='Hz';
parameters.invert_axis=1;
parameters.grid='LE2orientations+1+1';
parameters.rho0=state(spin_system,'L+','1H','cheap');
parameters.coil=state(spin_system,'L+','1H','cheap');
parameters.verbose=0;

% Simulation
fid=singlerot(spin_system,@acquire,parameters,'nmr');

% Apodization
fida=apodization(fid,'exp-1d',2);

% Fourier transform
spectruma=fftshift(fft(fida,parameters.zerofill));
% Plotting
figure(1); plot_1d(spin_system,real(spectruma),parameters);
end

ABC Spin System (Fig. 2e-f)

% 2D 1H MAS z-COSY or anti-z-COSY spectra of a single crystal with two different orientations
% computed using the FP formalism.
% Calculation time: depends on spin system.
% by LE, PM, BS from EPFL

function [fid]=mas_3spins_COSY()

sys.enable={’greedy’,’gpu’};
sys.isotopes={’1H’,’1H’,’1H’};

inter.coupling.eigs=cell(3,3);
inter.coupling.euler=cell(3,3);
inter.coupling.scalar=cell(3,3);

cscal=1.0;
inter.zeeman.eigs{1}=[4.0 4.0 4.0]*cscal;
inter.zeeman.eigs{2}=[3.6 3.6 3.6]*cscal;
inter.zeeman.eigs{10}=[12 12 12]*cscal;

inter.zeeman.euler{1}=[pi/7 pi/6 pi/11];
inter.zeeman.euler{2}=[pi/3 pi/13 pi/2];
inter.zeeman.euler{10}=[pi/3 pi/10 pi/2];

dscal=1.0;
inter.coupling.eigs{1,2}=[4 -2 -2]*dscal*1e3;
inter.coupling.eigs{1,3}=[6.6 -3.3 -3.3]*dscal*1e3;
inter.coupling.eigs{2,3}=[4.4 -2.2 -2.2]*dscal*1e3;

inter.coupling.euler{1,2}=[pi/6 pi/2 pi/20];
inter.coupling.euler{1,3}=[pi/4 pi/2 pi/3];
inter.coupling.euler{2,3}=[pi/3 pi/3 pi/2];

jscal=0.0;
inter.coupling.scalar{1,2}=10*jscal;
inter.coupling.scalar{1,3}=9*jscal;
inter.coupling.scalar{2,3}=5*jscal;

% Magnet field
sys.magnet=14;

% Basis set
bas.formalism=’sphten-liouv’;
bas.approximation=’none’;

% Algorithmic options
sys.tols.inter_cutoff=1.0;
sys.tols.prox_cutoff=100.0;
% Spinach housekeeping
spin_system=create(sys,inter);
spin_system=basis(spin_system,bas);

% Experiment setup
parameters.rate=10000;
parameters.axis=[1 1 1];
parameters.max_rank=5;
parameters.sweep=10000;
parameters.npoints=[2*1024 2*1024];
parameters.offset=4801.04;
parameters.spins={'1H'};
parameters.decouple={};
parameters.axis_units='Hz';
parameters.rho0=state(spin_system,'Lz','1H');
parameters.coil=state(spin_system,'L+','1H');
parameters.grid='2orientations';
parameters.verbose=0;
parameters.beta=3; %beta angle
parameters.antiz=1; %when 0 a ZQF or zCOSY is simulated, when 1 an
antizCOSY is simulated

% Simulation
fid=singlerot(spin_system,@pm_antizcosy_solids,parameters,'nmr');

end

Orientations File ('2orientations')

α = [0 0.3142]
β = [0 1.0472]
γ = [0 3.491]
weights = [1 1]
Mathematica Script

$Path =
    Append[$Path, "../Mathematica/SDv3.3.2/SpinDynamica"];
Needs["SpinDynamica"];

Two-spin system

SetSpinSystem[3];

Parameters;

\[ \begin{align*}
    \theta_1 &= 2 \pi 82.0; \ \theta_2 = 2 \pi 12.0; \ \theta_3 = 2 \pi 127.0; \\
    A_{2,2} &= 0; A_{2,-1} = 0; A_{2,1} = 0; A_{2,0} = 2000.0; \\
    B_{2,2} &= 0; B_{2,-1} = 0; B_{2,1} = 0; B_{2,0} = 4000.0; \\
    C_{2,2} &= 0; C_{2,-1} = 0; C_{2,1} = 0; C_{2,0} = 6000.0; \\
    aMR1 &= \pi / 20; bMR1 = \pi / 13; yMR1 = \pi / 7; \\
    aMR2 &= \pi / 7; bMR2 = \pi / 3; yMR2 = \pi / 5; \\
    aMR3 &= \pi / 8; bMR3 = \pi / 6; yMR3 = \pi / 10; \\
\end{align*} \]

\[ H_{\text{tot}}[t] := \theta_1 \text{opT}[1, \{1, 0\}] + \theta_2 \text{opT}[2, \{1, 0\}] + \theta_3 \text{opT}[3, \{1, 0\}] + \text{Sum}[A_{2,m} \text{WignerD}[2, \{m, m1\}][\{aMR1, bMR1, yMR1\}] \times \\
\quad \text{WignerD}[2, \{m1, 0\}][\{\text{wRot} t, \text{ArcTan}[\sqrt{2}2], 0\}] \times \text{opT}[\{1, 2\}, \{2, 0\}], \\
\quad \{m, -2, 2\}, \{m1, -2, 2\}] + \text{Sum}[B_{2,m} \text{WignerD}[2, \{m, m1\}][\{aMR2, bMR2, yMR2\}] \times \\
\quad \text{WignerD}[2, \{m1, 0\}][\{\text{wRot} t, \text{ArcTan}[\sqrt{2}2], 0\}] \times \text{opT}[\{1, 2\}, \{2, 0\}], \\
\quad \{m, -2, 2\}, \{m1, -2, 2\}] + \text{Sum}[C_{2,m} \text{WignerD}[2, \{m, m1\}][\{aMR3, bMR3, yMR3\}] \times \\
\quad \text{WignerD}[2, \{m1, 0\}][\{\text{wRot} t, \text{ArcTan}[\sqrt{2}2], 0\}] \times \text{opT}[\{2, 3\}, \{2, 0\}], \{m, -2, 2\}, \{m1, -2, 2\}] // \text{Chop} \]

First order

\[ \text{Ham1st}[\text{wRot}] := \frac{\text{wRot}}{2\pi} \text{Integrate}[H_{\text{tot}}[t], \{t, 0, \frac{2\pi}{\text{wRot}}\}] \]

\text{ExpressOperator}[\text{Operator} \circ \text{Ham1st}[\text{wRot}]]
Second order

\[
\begin{align*}
\text{commut2}[t_1, t_2] & := \text{MatrixRepresentation}[\text{Htot}[t_2]].\text{MatrixRepresentation}[\text{Htot}[t_1]] - \\
& \quad \text{MatrixRepresentation}[\text{Htot}[t_1]].\text{MatrixRepresentation}[\text{Htot}[t_2]]; \\
\text{Ham2nd}[\text{uRot}] & := \frac{\text{uRot}}{2\pi} \text{Integrate}\left[\text{Integrate}\left[\text{commut2}[t_1, t_2], \{t_1, 0, t_2\}, \{t_2, 0, t_2\}\right], \{t_2, 0, 2\pi\}\right] \\
& \quad \text{ExpressOperator}[\text{Operator} @ \text{Ham2nd}[\text{uRot}], \text{CartesianProductOperatorBasis}[]] // \text{Chop} // \text{FullSimplify} \\
\text{secularization1} & = \text{Secularize}[\text{ExpressOperator}[\text{Operator} @ \text{Ham2nd}[\text{uRot}]], \\
& \quad 2\pi 82.0 \text{ opI}[1, "z"] + 2\pi 12.0 \text{ opI}[2, "z"] + 2\pi 127.0 \text{ opI}[3, "z"] + 2\pi 44.0] \\
\end{align*}
\]

Third order

\[
\begin{align*}
\text{commut12}[t_1, t_2] & := \text{MatrixRepresentation}[\text{Htot}[t_2]].\text{MatrixRepresentation}[\text{Htot}[t_1]] - \\
& \quad \text{MatrixRepresentation}[\text{Htot}[t_1]].\text{MatrixRepresentation}[\text{Htot}[t_2]]; \\
\text{commut23}[t_2, t_3] & := \text{MatrixRepresentation}[\text{Htot}[t_3]].\text{MatrixRepresentation}[\text{Htot}[t_2]] - \\
& \quad \text{MatrixRepresentation}[\text{Htot}[t_2]].\text{MatrixRepresentation}[\text{Htot}[t_3]]; \\
\text{commut123}[t_1, t_2, t_3] & := \text{MatrixRepresentation}[\text{Htot}[t_3]].\text{MatrixRepresentation}[\text{Htot}[t_2]] - \\
\text{commut12}[t_1, t_2, t_3].\text{MatrixRepresentation}[\text{Htot}[t_3]]; \\
\text{secularization2} & = \text{Secularize}[\%[, \\
& \quad 2\pi 82.0 \text{ opI}[1, "z"] + 2\pi 12.0 \text{ opI}[2, "z"] + 2\pi 127.0 \text{ opI}[3, "z"] + 2\pi 44.0]} \\
\end{align*}
\]
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