Supplementary Information

Floquet Theory and Average Hamiltonian Theory Revisited:
Equivalence, Convergence and Applications to NMR

S1 Simulation of spectra

This section provides details on how the NMR spectra are calculated. This can be done both for stroboscopic measurements (time increment $\tau = T$) and for additional intra-stroboscopic measurements, i.e., $\tau = T/\alpha$ with $\alpha \in \mathbb{N}$.

For simplicity, $U(t) := U(t_0 + t, t_0)$ is set, the detection operator is denoted by $\mathcal{S}$, and the initial density operator by $\rho := \rho(t_0)$. The time-dependent measurement of $\mathcal{S}$ is the quantum mechanical average, i.e., $\mathcal{S}(t) := \langle \mathcal{S}(t) \rangle$, which is given for general time increment τ by

$$\mathcal{S}(n\tau) = \mathrm{Tr}\{U(n\tau)\rho U^\dagger(n\tau)\mathcal{S}\}\,,\; n \in \mathbb{Z}\,. \tag{S1}$$

The smaller τ, the wider is the corresponding spectrum, which is defined by

$$\mathcal{S}(\omega) = \frac{1}{\alpha}\sum_{n=0}^{\infty} e^{in\omega\tau}\mathcal{S}(n\tau)\,,\; \omega \in [-\frac{\pi}{\tau}, \frac{\pi}{\tau})\,. \tag{S2}$$

The line shapes are normalized such that the maximum absolute value of the exact spectrum is one.

S1.1 Time increment $\tau = T$

The Floquet theorem implies that the propagator fulfills $U(nT) = (U(T))^n$ with $n \in \mathbb{Z}$. Let $\{|j^u\rangle\}_j$ be the orthonormalized eigenstates of $U(T)$ with corresponding eigenvalues $\{\kappa_j\}_j$. The latter are directly connected to the eigenvalues $\{\lambda_j\}_j$ of the effective Hamiltonian F via $\kappa_j = e^{-i\lambda_j T}$. The eigenvectors $\{|j\rangle\}_j$ of F are given by $|j\rangle = e^{+i\Lambda(t_0)}|j^u\rangle$. The eigenvalue equation can be used to re-write $\mathcal{S}(nT)$

$$\mathcal{S}(nT) = \sum_{j,k} e^{-i(\lambda_j-\lambda_k)nT}\langle j^u|\rho|k^u\rangle\langle k^u|\mathcal{S}|j^u\rangle\,. \tag{S3}$$

This relation is inserted into Eq. (S2). The following step includes a continuation to the imaginary plane by $\omega \to \omega + i\eta$ with $\eta > 0$, which ensures convergence of the infinite sum,

$$\mathcal{S}(\omega) = \sum_{j,k}\langle j^u|\rho|k^u\rangle\langle k^u|\mathcal{S}|j^u\rangle\frac{1}{1 - e^{-\eta T}e^{i(\omega-\lambda_j+\lambda_k)T}}\,,\; \omega \in [-\frac{\pi}{T}, \frac{\pi}{T})\,. \tag{S4}$$

This exponential line broadening smoothes Delta-shaped resonances into well-displayable Lorentzian line shapes, which have a full width at half maximum of 2η in angular frequencies.

S1.2 Time increment $\tau = T/\alpha$

The spectrum in Eq. (S2) for non-stroboscopic measurements can be re-written as

$$\mathcal{S}(\omega) = \frac{1}{\alpha}\sum_{n=0}^{\infty}\sum_{k=0}^{\alpha-1} e^{i\omega(nT+k\tau)}\mathcal{S}(nT+k\tau)\,. \tag{S5}$$

The stroboscopic and intra-stroboscopic dynamics can be split up via

$$U(nT+k\tau) = U(k\tau)(U(T))^n\,,\; n\in\mathbb{N}^0\,,\; k=0,1,\ldots,n-1 \tag{S6}$$

because $U(t,t') = U(t+T,t'+T)$ holds for periodic Hamiltonians. The time-dependent expectation value of $\mathcal{S}$ then simplifies to

$$\mathcal{S}(nT+k\tau) = \sum_{i,j,l,m} e^{-i(\lambda_j-\lambda_l)nT}\langle i^u|U(k\tau)|j^u\rangle\langle l^u|U^\dagger(k\tau)|m^u\rangle\langle j^u|\rho|l^u\rangle\langle m^u|\mathcal{S}|i^u\rangle\,. \tag{S7}$$

For convenience, we define the ω-dependent factor

$$\Psi_{ijlm} := \frac{1}{\alpha}\sum_{k=0}^{\alpha-1} e^{i\omega k\tau}\langle i^u|U(k\tau)|j^u\rangle\langle l^u|U^\dagger(k\tau)|m^u\rangle \tag{S8}$$

and provide an expression for $\mathcal{S}(\omega)$ similar to the one found for stroboscopic observations

$$\mathcal{S}(\omega) = \sum_{ijlm}\Psi_{ijlm}\langle m^u|\mathcal{S}|i^u\rangle\langle j^u|\rho|l^u\rangle\frac{1}{1-e^{-\eta T}e^{i(\omega-\lambda_j+\lambda_l)T}}\,,\; \omega\in[-\frac{\alpha\pi}{T},\frac{\alpha\pi}{T})\,. \tag{S9}$$

S2 Additional material on the Bloch–Siegert shift

Supplementarily to the explorations on the Bloch–Siegert shift in our work, Figs. S1 and S2 provide the detection signals in the y- and z-direction.

S3 Reduced Wigner rotation matrix elements

We follow the zyz convention for Wigner rotations as it is common in NMR [2, 3]. Note that there are also different rotation conventions in use and, thus, their interim results may look different. The corresponding reduced Wigner rotation matrix elements can be found in Tab. S1. The full Wigner rotation matrix elements for rank-2 tensors are then given by

$$D^2_{m'm}(\alpha,\beta,\gamma) = e^{-im'\alpha}d^2_{m',m}(\beta)e^{-im\gamma}\,. \tag{S10}$$

S4 Remarks on the powder average

For a two-spin crystallite under magic-angle spinning, the powder average over the angles β and γ is sufficient, i.e., $\alpha = 0$ can be set without loss of generality. Starting from the MAS

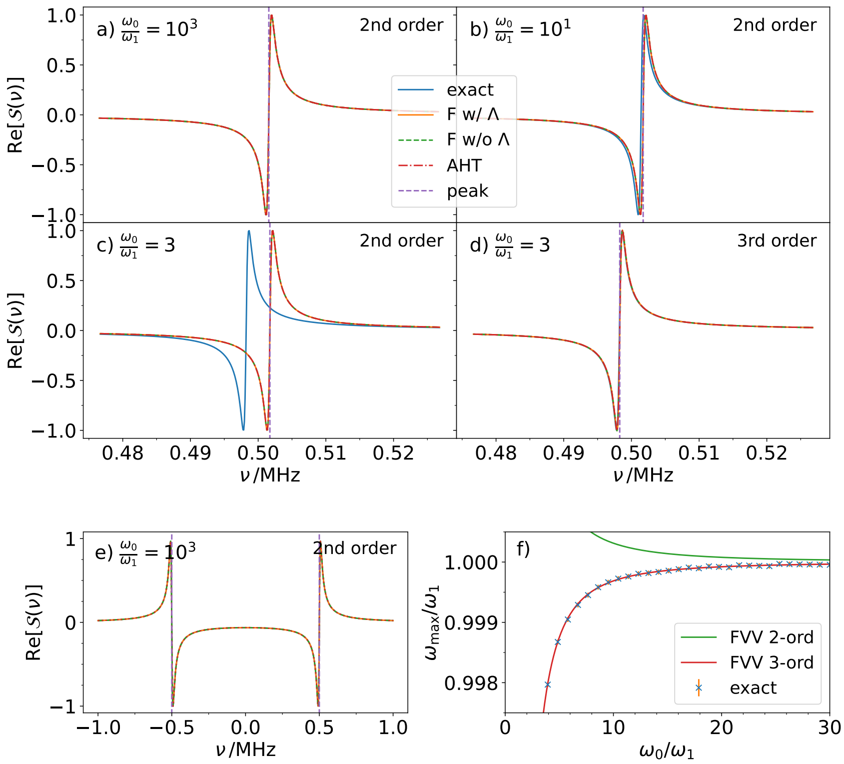

Fig. S1: The Bloch–Siegert shift [1] of a single-spin system under a linear-polarized resonant radiofrequency (rf) field. Results according to AHT and FVV with and without kick operator Λ are compared to the numerically exact outcome. The detection operator is $\mathcal{S} = S^y$, and the initial density operator is $\rho = S^z$. The amplitude of the rf field is set to $\omega_1/(2\pi) = 0.5\,\text{MHz}$, and the resonance frequency ω_0 is varied. The broadening parameter is $\eta/(2\pi) = 0.4\,\text{kHz}$ in a)-d), and $\eta/(2\pi) = 8\,\text{kHz}$ in e). An overview of the spectrum is displayed in e). In a)-d), excerpts highlighting the actual Bloch–Siegert shift for different ratios ω_0/ω_1 are shown. The purple dashed line corresponds to the peak predicted by FVV.

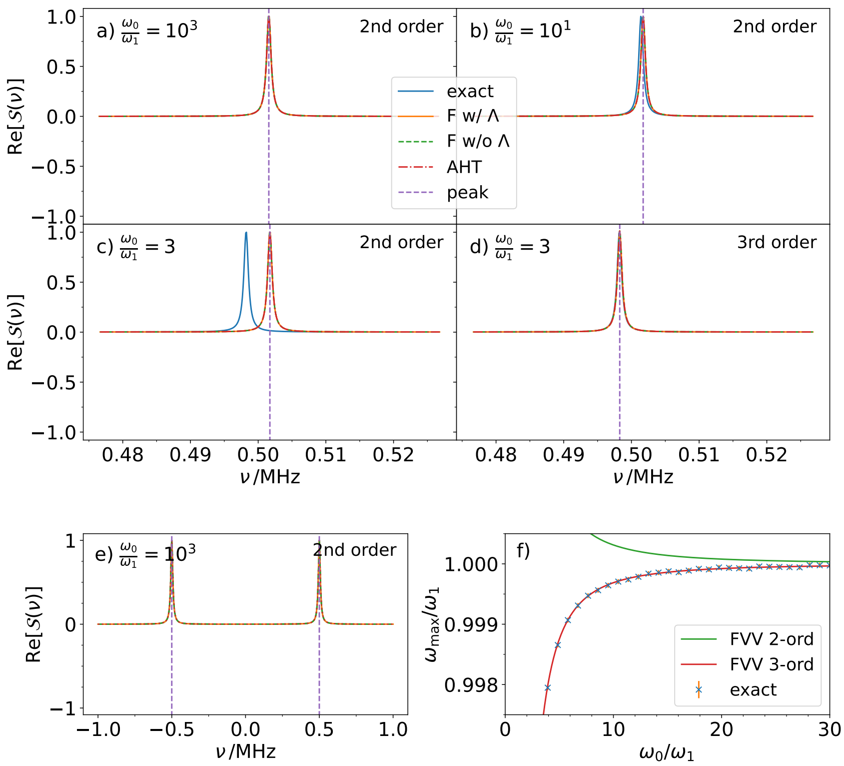

Fig. S2: Bloch–Siegert shift [1] of a single-spin system under a linear-polarized resonant radiofrequency (rf) field. Results according to AHT and FVV with and without kick operator Λ are compared to the numerically exact outcome. The detection operator is $\mathcal{S} = S^z$, and the initial density operator is $\rho = S^z$. The amplitude of the rf field is set to $\omega_1/(2\pi) = 0.5\,\text{MHz}$, and the resonance frequency ω_0 is varied. The broadening parameter is $\eta/(2\pi) = 0.4\,\text{kHz}$ in a)-d), and $\eta/(2\pi) = 8\,\text{kHz}$ in e). An overview of the spectrum is displayed in e). In a)-d), excerpts highlighting the actual Bloch–Siegert shift for different ratios ω_0/ω_1 are shown. The purple dashed line corresponds to the peak predicted through FVV.

Table S1: Reduced Wigner rotation matrix elements $d^{\ell=2}_{m',m}(\beta)$ in the zyz convention for rank-2 tensors, adapted from Refs. [2, 3].

m'	m = -2	-1	0	1	2
-2	$\left(\frac{1+\cos\beta}{2}\right)^2$	$\frac{1+\cos\beta}{2}\sin\beta$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$\frac{1-\cos\beta}{2}\sin\beta$	$\left(\frac{1-\cos\beta}{2}\right)^2$
-1	$-\frac{1+\cos\beta}{2}\sin\beta$	$\cos^2\beta-\frac{1-\cos\beta}{2}$	$\sqrt{\frac{3}{8}}\sin(2\beta)$	$\frac{1+\cos\beta}{2}-\cos^2\beta$	$\frac{1-\cos\beta}{2}\sin\beta$
0	$\sqrt{\frac{3}{8}}\sin^2\beta$	$-\sqrt{\frac{3}{8}}\sin(2\beta)$	$\frac{3\cos^2\beta-1}{2}$	$\sqrt{\frac{3}{8}}\sin(2\beta)$	$\sqrt{\frac{3}{8}}\sin^2\beta$
1	$-\frac{1-\cos\beta}{2}\sin\beta$	$\frac{1+\cos\beta}{2}-\cos^2\beta$	$-\sqrt{\frac{3}{8}}\sin(2\beta)$	$\cos^2\beta-\frac{1-\cos\beta}{2}$	$\frac{1+\cos\beta}{2}\sin\beta$
2	$\left(\frac{1-\cos\beta}{2}\right)^2$	$-\frac{1-\cos\beta}{2}\sin\beta$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$-\frac{1+\cos\beta}{2}\sin\beta$	$\left(\frac{1+\cos\beta}{2}\right)^2$

NMR Hamiltonian in our work, this can be seen if

$$H_{12}^{\mathrm{PAS}} = \frac{\delta_{12}}{2}\{3S_1^zS_2^z - \vec{S}_1\cdot\vec{S}_2\} \tag{S11a}$$

$$H_{12}^{\mathrm{LAB}} = \sum_{m'=-2}^{2} D^2_{m',0}(-\omega_\mathrm{r}t,-\theta_\mathrm{m},0)\sum_{m=-2}^{2} D^2_{m,m'}(\alpha,\beta,\gamma)D^2_{0,m}(0,-\theta_{12}=0,-\phi_{12}=0)H_{12}^{\mathrm{PAS}} \tag{S11b}$$

$$= \sum_{m'=-2}^{2} D^2_{m',0}(-\omega_\mathrm{r}t,-\theta_\mathrm{m},0)D^2_{0,m'}(\alpha,\beta,\gamma)H_{12}^{\mathrm{PAS}} \tag{S11c}$$

$$= \sum_{m'=-2}^{2} e^{im'\omega_\mathrm{r}t}d^2_{m',0}(-\theta_\mathrm{m})e^{-i\cdot 0\cdot\alpha}d^2_{0,m'}(\beta)e^{-im'\gamma}H_{12}^{\mathrm{PAS}}\,. \tag{S11d}$$

Here, δ_{12} is the anisotropy of the dipolar coupling, the Wigner rotation matrix $D^2_{m,m'}$ is given in Eq. (S10), θ_m is the magic angle, and the rotation frequency is denoted by ω_r.

The ZCW scheme [4, 5], that we employ for the orientational average, is summarized as follows: The goal is to find a set of p angular triples $\{\alpha_i,\beta_i,\gamma_i\}$ that is tailored to approximate an average of a function f by replacing it through a sum

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}\frac{f(\alpha,\beta,\gamma)}{8\pi^2}\sin\beta\,\mathrm{d}\alpha\mathrm{d}\beta\mathrm{d}\gamma \approx \sum_{i=1}^{p}\frac{f(\alpha_i,\beta_i,\gamma_i)}{p}\,. \tag{S12}$$

According to the algorithm, an integer $M\geq 2$ is chosen, and for $\lfloor x\rfloor$ being the floor function, the fractional part of the real number x is defined by $\{x\} := x-\lfloor x\rfloor \in [0,1)$. For an average over two angles, i.e., $\alpha_i = 0\,\forall\, i$, the remaining angular pairs are computed by

$$f_0 = 8\,,\ f_1 = 13\,,\ f_{i+2} = f_{i+1}+f_i\,,\ 2\leq i\leq M\,, \tag{S13a}$$

$$\beta_j = \arccos\left(2\left\{\frac{jf_M}{f_{M+2}}\right\}-1\right)\in[0,\pi)\,, \tag{S13b}$$

$$\gamma_j = 2\pi\left\{\frac{j}{f_{M+2}}\right\}\in[0,2\pi)\,,\ 0\leq j\leq f_{M+2}-1\,. \tag{S13c}$$

Consequently, the number of orientations is f_{M+2} in this case. This rule cannot be extended including the third angle α as well. For the powder average over three angles, we used the optimum vector resulting from the Zaremba [6] method for 1154 samples, which is given in [4].

S5 Mathematica calculations to check AHT expressions

To check the validity of our expressions for the average Hamiltonian, we compared the results generated by the integral form of the first four orders of AHT (Eqs. 17a,c,e and B3) with the outcome for the Fourier series expressions (Eqs. 31a-f and B4) for a dipolar-coupled two-spin system under MAS. All four orders of the average Hamiltonian give the same results. The Mathematica code used for the validations is included here.

AHT Calculation for a dipolar-coupled two-spin system with chemical shifts

Load package for analytical spin-operator calculations

In[1]:=
```
<< NMR11/StartUpNMR.m
```

NMR with Mathematica

Version 1.1

Marlies Brinksma

Email: mabi@solidmr.kun.nl


```
/Applications/Wolfram.app/Contents/AddOns/Applications/NMR11/Spinsystem.m loaded...
```

NormalForm : $Pre is set to: CheckTimes

```
/Applications/Wolfram.app/Contents/AddOns/Applications/NMR11/NormalForm.m loaded...
/Applications/Wolfram.app/Contents/AddOns/Applications/NMR11/SOFunctions.m loaded...
```

SetDelayed : Tag SquareMatrixQ in SquareMatrixQ [mat _?MatrixQ] is Protected.

SetDelayed : Tag SquareMatrixQ in SquareMatrixQ [expr _] is Protected.

```
/Applications/Wolfram.app/Contents/AddOns/Applications/NMR11/SpinMatrix.m loaded...
/Applications/Wolfram.app/Contents/AddOns/Applications/NMR11/QMFunctions.m loaded...
/Applications/Wolfram.app/Contents/AddOns/Applications/NMR11/NMRFunctions.m loaded...
```

Set up the time-dependent Hamiltonian

In[2]:=
```
Ham[t_] := Ω1 S[1, z] + Ω2 S[2, z] + Sum[ω12[n] Exp[I n ωr t]
    (2 S[1, z] × S[2, z] - S[1, x] × S[2, x] - S[1, y] × S[2, y]), {n, {-2, -1, 1, 2}}]
```

Spinsystem : Spin 1 has been registered...

Spinsystem : Spin 2 has been registered...

In[3]:=
```
Ham[t1]
```

Out[3]=

$$S_{1,z}\,\Omega_1 + S_{2,z}\,\Omega_2 + e^{-2\,i\,t1\,\omega_r}\,(-S_{1,x}\,S_{2,x} - S_{1,y}\,S_{2,y} + 2\,S_{1,z}\,S_{2,z})\,\omega_{12}[-2] +$$
$$e^{-i\,t1\,\omega_r}\,(-S_{1,x}\,S_{2,x} - S_{1,y}\,S_{2,y} + 2\,S_{1,z}\,S_{2,z})\,\omega_{12}[-1] +$$
$$e^{i\,t1\,\omega_r}\,(-S_{1,x}\,S_{2,x} - S_{1,y}\,S_{2,y} + 2\,S_{1,z}\,S_{2,z})\,\omega_{12}[1] +$$
$$e^{2\,i\,t1\,\omega_r}\,(-S_{1,x}\,S_{2,x} - S_{1,y}\,S_{2,y} + 2\,S_{1,z}\,S_{2,z})\,\omega_{12}[2]$$

Calculate the integral form of the first four orders of AHT

In[4]:=
```
H1 = ωr / (2 π) Integrate[Ham[t1], {t1, 0, 2 π / ωr}]
```

Out[4]= $S_{1,z}\,\Omega_1 + S_{2,z}\,\Omega_2$

In[5]:=
```
H2 = -I ωr / (4 π) Integrate[
    Integrate[Commutator[Ham[t2], Ham[t1]], {t1, 0, t2}], {t2, 0, 2 π / ωr}];
FullSimplify[H2]
```

Out[6]=
$$\frac{i\,(S_{1,y}\,S_{2,x} - S_{1,x}\,S_{2,y})\,(\Omega_1 - \Omega_2)\,(\omega_{12}[-2] + 2\,\omega_{12}[-1] - 2\,\omega_{12}[1] - \omega_{12}[2])}{2\,\omega_r}$$

In[7]:=
```
H3 = -1 ωr / (12 π) Integrate[
    Integrate[Integrate[Commutator[Ham[t3], Commutator[Ham[t2], Ham[t1]]] +
       Commutator[Commutator[Ham[t3], Ham[t2]], Ham[t1]],
      {t1, 0, t2}], {t2, 0, t3}], {t3, 0, 2 π / ωr}];
FullSimplify[H3]
```

Out[8]=
$$\frac{1}{16\,\omega_r^2}(\Omega_1 - \Omega_2)\Big(4\,S_{1,x}\,S_{2,x}\,(\Omega_1 - \Omega_2)\,(\omega_{12}[-2] + 4\,(\omega_{12}[-1] + \omega_{12}[1]) + \omega_{12}[2]) + 4\,S_{1,y}\,S_{2,y}\,(\Omega_1 - \Omega_2)\,(\omega_{12}[-2] + 4\,(\omega_{12}[-1] + \omega_{12}[1]) + \omega_{12}[2]) + (S_{1,z} - S_{2,z})\Big(\omega_{12}[-2]^2 + 4\,\omega_{12}[-1]^2 + 4\,\omega_{12}[-2]\,(\omega_{12}[-1] - \omega_{12}[1] - \omega_{12}[2]) + (2\,\omega_{12}[1] + \omega_{12}[2])^2 - 4\,\omega_{12}[-1]\,(4\,\omega_{12}[1] + \omega_{12}[2])\Big)\Big)$$

In[9]:=
```
H4 = I ωr / (24 π) Integrate[Integrate[Integrate[Integrate[
       Commutator[Ham[t4], Commutator[Ham[t3], Commutator[Ham[t1], Ham[t2]]]],
       {t4, 0, t3}], {t3, 0, t2}], {t2, 0, t1}], {t1, 0, 2 π / ωr}];
H4 = H4 + I ωr / (24 π) Integrate[Integrate[Integrate[Integrate[Commutator[Ham[t1],
         Commutator[Ham[t4], Commutator[Ham[t3], Ham[t2]]]], {t4, 0, t3}],
       {t3, 0, t2}], {t2, 0, t1}], {t1, 0, 2 π / ωr}];
H4 = H4 + I ωr / (24 π) Integrate[Integrate[Integrate[Integrate[Commutator[Ham[t1],
         Commutator[Ham[t2], Commutator[Ham[t3], Ham[t4]]]], {t4, 0, t3}],
       {t3, 0, t2}], {t2, 0, t1}], {t1, 0, 2 π / ωr}];
H4 = H4 + I ωr / (24 π) Integrate[Integrate[Integrate[Integrate[Commutator[Ham[t2],
         Commutator[Ham[t3], Commutator[Ham[t4], Ham[t1]]]], {t4, 0, t3}],
       {t3, 0, t2}], {t2, 0, t1}], {t1, 0, 2 π / ωr}];
FullSimplify[H4]
```

Out[13]=
$$\frac{1}{48\,\omega_r^3}\,i\,(S_{1,y}\,S_{2,x} - S_{1,x}\,S_{2,y})\,(\Omega_1 - \Omega_2)\Big(\omega_{12}[-2]^3 + 6\,\omega_{12}[-2]^2\,\omega_{12}[-1] + 12\,\omega_{12}[-2]\,\omega_{12}[-1]^2 + 8\,\omega_{12}[-1]^3 - 6\,\omega_{12}[-2]^2\,\omega_{12}[1] - 48\,\omega_{12}[-2]\,\omega_{12}[-1]\,\omega_{12}[1] - 72\,\omega_{12}[-1]^2\,\omega_{12}[1] + 72\,\omega_{12}[-1]\,\omega_{12}[1]^2 - 8\,\omega_{12}[1]^3 + 6\,\Omega_1^2\,(\omega_{12}[-2] + 8\,\omega_{12}[-1] - 8\,\omega_{12}[1] - \omega_{12}[2]) - 12\,\Omega_1\,\Omega_2\,(\omega_{12}[-2] + 8\,\omega_{12}[-1] - 8\,\omega_{12}[1] - \omega_{12}[2]) + 6\,\Omega_2^2\,(\omega_{12}[-2] + 8\,\omega_{12}[-1] - 8\,\omega_{12}[1] - \omega_{12}[2]) - 3\,(\omega_{12}[-2] - 2\,\omega_{12}[1])\,(3\,\omega_{12}[-2] + 8\,\omega_{12}[-1] - 2\,\omega_{12}[1])\,\omega_{12}[2] + 3\,(3\,\omega_{12}[-2] + 2\,\omega_{12}[-1] - 2\,\omega_{12}[1])\,\omega_{12}[2]^2 - \omega_{12}[2]^3\Big)$$

Calculate the commutator form of the first four orders of AHT

In[14]:=
```
HamC = Ham[t] //. {Exp[-2 I t ωr] → xr^-2,
   Exp[-1 I t ωr] → xr^-1, Exp[1 I t ωr] → xr^1, Exp[2 I t ωr] → xr^2}
```

Out[14]=

$$S_{1,z}\,\Omega_1 + S_{2,z}\,\Omega_2 + \frac{(-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[-2]}{xr^2} + \frac{(-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[-1]}{xr} + xr\,(-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[1] + xr^2\,(-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[2]$$

In[15]:=
```
Fcoeff = CoefficientList[HamC * xr^2, {xr}]
```

Out[15]=

$$\{(-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[-2],\ (-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[-1],\ S_{1,z}\,\Omega_1 + S_{2,z}\,\Omega_2,\ (-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[1],\ (-S_{1,x} S_{2,x} - S_{1,y} S_{2,y} + 2 S_{1,z} S_{2,z})\,\omega_{12}[2]\}$$

In[16]:=
```
Hn = Table[0, {n, -10, 10}]
```

Out[16]=
```
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
```

In[17]:=
```
For[k = -2, k ≤ 2, k = k + 1, Hn[[k]] = Fcoeff[[k + 3]]]
```

In[18]:=
```
H1S = Hn[[0]]
```

Out[18]=

$$S_{1,z}\,\Omega_1 + S_{2,z}\,\Omega_2$$

In[19]:=
```
H2S = 0;
For[k = -2, k ≤ 2, k = k + 1,
 If[k ≠ 0,
   H2S = H2S + 1 / 2 * Commutator[Hn[[k]], Hn[[-k]]] / (k * ωr);
   H2S = H2S + Commutator[Hn[[0]], Hn[[k]]] / (k * ωr);
  ];
]
```

Part : The expression NormalForm`Private`TempTimes [−1, 3] cannot be used as a part specification.

Part : The expression NormalForm`Private`TempTimes [−1, 3] cannot be used as a part specification.

Part : The expression NormalForm`Private`TempTimes [−1, 3] cannot be used as a part specification.

General : Further output of Part::pkspec1 will be suppressed during this calculation.

In[21]:=
```
FullSimplify[H2S]
```

Out[21]=

$$\frac{i\,(S_{1,y} S_{2,x} - S_{1,x} S_{2,y})\,(\Omega_1 - \Omega_2)\,(\omega_{12}[-2] + 2\,\omega_{12}[-1] - 2\,\omega_{12}[1] - \omega_{12}[2])}{2\,\omega_r}$$

In[22]:=
```
H3S = 0;
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 If[k1 ≠ 0,
  H3S = H3S + 2 / 3 * Commutator[Hn[[k1]], Commutator[Hn[[0]], Hn[[-k1]]]] / (k1 * ωr) ^ 2;
 ]
]
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
  If[k1 ≠ 0 && k2 ≠ 0 && Abs[k1 - k2] ≤ 2,
   H3S = H3S + 1 / 3 *
       Commutator[Hn[[k1]], Commutator[Hn[[k2 - k1]], Hn[[-k2]]]] / (k1 * k2 * ωr * ωr);
  ]
 ]
]
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
  If[k1 ≠ 0 && k2 ≠ 0,
   H3S = H3S +
      1 / 2 * Commutator[Hn[[k2]], Commutator[Hn[[-k1]], Hn[[k1]]]] / (k1 * k2 * ωr * ωr);
  ]
 ]
]
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
  If[k2 ≠ 0 && k2 ≠ -k1,
   H3S =
     H3S + Commutator[Hn[[k1]], Commutator[Hn[[k2]], Hn[[0]]]] / ((k1 + k2) * k2 * ωr * ωr);
  ]
 ]
]
```

In[27]:=
```
FullSimplify[H3S]
```

Out[27]=

$$\frac{1}{16\,\omega_r^2}(\Omega_1-\Omega_2)\Big(4\,S_{1,x}\,S_{2,x}\,(\Omega_1-\Omega_2)\,(\omega_{12}[-2]+4\,(\omega_{12}[-1]+\omega_{12}[1])+\omega_{12}[2])+ 4\,S_{1,y}\,S_{2,y}\,(\Omega_1-\Omega_2)\,(\omega_{12}[-2]+4\,(\omega_{12}[-1]+\omega_{12}[1])+\omega_{12}[2])+ (S_{1,z}-S_{2,z})\,\big(\omega_{12}[-2]^2+4\,\omega_{12}[-1]^2+4\,\omega_{12}[-2]\,(\omega_{12}[-1]-\omega_{12}[1]-\omega_{12}[2])+ (2\,\omega_{12}[1]+\omega_{12}[2])^2-4\,\omega_{12}[-1]\,(4\,\omega_{12}[1]+\omega_{12}[2])\big)\Big)$$

```
In[28]:= ω3 = ωr * ωr * ωr;
H4S = 0;
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 && k1 + k2 ≠ 0,
     For[k3 = -2, k3 ≤ 2, k3 = k3 + 1,
      If[k3 ≠ 0 && k3 + k2 + k1 ≠ 0,
       H4S = H4S + Commutator[Commutator[Hn⟦k1⟧, Hn⟦k2⟧],
             Commutator[Hn⟦k3⟧, Hn⟦-k1 - k2 - k3⟧]] / (24 * (
                k1 + k2 + k3) * (k1 + k2) * k1 * ω3)
           + Commutator[Hn⟦k1⟧, Commutator[Hn⟦k2⟧,
              Commutator[Hn⟦k3⟧, Hn⟦-k1 - k2 - k3⟧]]] / (24 * k1 * k2 * k3 * ω3)
           + Commutator[Hn⟦-k1 - k2 - k3⟧, Commutator[Hn⟦k3⟧,
              Commutator[Hn⟦k1⟧, Hn⟦k2⟧]]] / (6 * k1 * (k1 + k2) * (k1 + k2 + k3) * ω3);
      ]]]]]];

In[31]:= For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 && k1 + k2 ≠ 0,
     For[k3 = -6, k3 ≤ 6, k3 = k3 + 1,
      If[k3 ≠ 0 && k3 - k2 - k1 ≠ 0,
       H4S = H4S + Commutator[Hn⟦0⟧, Commutator[Hn⟦k1⟧, Commutator[Hn⟦k2⟧,
                Hn⟦k3 - k2 - k1⟧]]] * (2 * k2 - k1) / (6 * k1 * k2 * k3 * (k1 + k2) * ω3)
           + Commutator[Hn⟦k3 - k2 - k1⟧, Commutator[Hn⟦0⟧,
              Commutator[Hn⟦k1⟧, Hn⟦k2⟧]]] / (4 * (k3 - k2 - k1) * (k1 + k2) * k2 * ω3)
           + Commutator[Commutator[Hn⟦k2⟧, Hn⟦k1⟧], Commutator[
              Hn⟦k3 - k2 - k1⟧, Hn⟦0⟧]] / (4 * k2 * (k1 + k2) * (k3 - k1 - k2) * ω3)
           + Commutator[Hn⟦k1⟧, Commutator[Hn⟦k3 - k1 - k2⟧,
              Commutator[Hn⟦0⟧, Hn⟦k2⟧]]] / (6 * k1 * (k3 - k2 - k1) * k2 * ω3);
      ]]]]]];

In[32]:= For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 ,
     For[k3 = -2, k3 ≤ 2, k3 = k3 + 1,
      If[k3 ≠ 0,
       H4S = H4S + Commutator[Hn⟦k3⟧, Commutator[Hn⟦k1⟧,
              Commutator[Hn⟦-k1 - k2⟧, Hn⟦k2⟧]]] / (3 * k1 * k2 * k3 * ω3);
      ]]]]]];
```

```
In[33]:= For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
           If[k1 ≠ 0,
            For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
             If[k2 ≠ 0 ,
              For[k3 = -4, k3 ≤ 4, k3 = k3 + 1,
               If[k3 ≠ 0 && k3 - k2 ≠ 0,
                H4S = H4S + Commutator[Hn⟦k3 - k2⟧, Commutator[Hn⟦k2⟧,
                      Commutator[Hn⟦k1⟧, Hn⟦-k1⟧]]] / (4 * (k3 - k2) * k2 * k1 * ω3)
                   + Commutator[Commutator[Hn⟦k1⟧, Hn⟦-k1⟧],
                     Commutator[Hn⟦k2⟧, Hn⟦k3 - k2⟧]] / (4 * k1 * k2 * k3 * ω3);
               ]]]]]];

In[34]:= For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
           If[k1 ≠ 0,
            For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
             If[k2 ≠ 0 ,
              H4S = H4S + Commutator[Hn⟦k1⟧, Commutator[Hn⟦-k1⟧,
                    Commutator[Hn⟦-k2⟧, Hn⟦k2⟧]]] * 3 / (8 * k2 * k1 * k1 * ω3);
             ]]]];

In[35]:=
         For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
          If[k1 ≠ 0,
           For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
            If[k2 ≠ 0 && k1 + k2 ≠ 0,
             H4S = H4S + Commutator[Hn⟦k1⟧, Commutator[Hn⟦0⟧,
                   Commutator[Hn⟦k2⟧, Hn⟦-k1 - k2⟧]]] / (2 * k1 * k1 * k2 * ω3)
                + Commutator[Hn⟦k1⟧,
                  Commutator[Hn⟦-k1 - k2⟧, Commutator[Hn⟦0⟧, Hn⟦k2⟧]]] *
                 (2 * k1 + k2) / (6 * k1 * k2 * k2 * (k1 + k2) * ω3)
                + Commutator[Commutator[Hn⟦-k1 - k2⟧, Hn⟦0⟧],
                  Commutator[Hn⟦k1⟧, Hn⟦k2⟧]] / (3 * k1 * (k1 + k2) * (k1 + k2) * ω3);
            ]]]]

In[36]:= For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
           If[k1 ≠ 0,
            For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
             If[k2 ≠ 0 ,
              H4S = H4S + Commutator[Hn⟦0⟧, Commutator[Hn⟦k1⟧,
                    Commutator[Hn⟦k2⟧, Hn⟦-k1⟧]]] * (6 * k1 + k2) / (12 * k1 * k1 * k2 * k2 * ω3)
                 + Commutator[Commutator[Hn⟦k1⟧, Hn⟦-k1⟧],
                   Commutator[Hn⟦k2⟧, Hn⟦0⟧]] / (2 * k1 * k2 * k2 * ω3)
                 + Commutator[Hn⟦k2⟧,
                   Commutator[Hn⟦k1⟧, Commutator[Hn⟦-k1⟧, Hn⟦0⟧]]] / (6 * k2 * k1 * k1 * ω3)
                 + Commutator[Hn⟦k1⟧,
                   Commutator[Hn⟦k2⟧, Commutator[Hn⟦-k1⟧, Hn⟦0⟧]]] / (6 * k2 * k1 * k1 * ω3);
             ]]]];
```

In[37]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 ,
     H4S = H4S + Commutator[Hn⟦k1⟧,
          Commutator[Hn⟦0⟧, Commutator[Hn⟦0⟧, Hn⟦k2⟧]]] / (4 * k2 * k2 * k1 * ω3)
        + Commutator[Commutator[Hn⟦k2⟧, Hn⟦0⟧],
          Commutator[Hn⟦k1⟧, Hn⟦0⟧]] / (4 * k2 * k2 * k1 * ω3);
    ]]]];
```

In[38]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -4, k2 ≤ 4, k2 = k2 + 1,
    If[k2 ≠ 0 && k2 - k1 ≠ 0,
     H4S = H4S +
        Commutator[Hn⟦0⟧, Commutator[Hn⟦k1⟧, Commutator[Hn⟦0⟧, Hn⟦k2 - k1⟧]]] *
         (4 * k1 * k2 - 2 * k1 * k1 - k2 * k2) / (2 * k1 * (k2 - k1) * (k2 - k1) * k2 * k2 * ω3)
        + Commutator[Hn⟦k2 - k1⟧, Commutator[Hn⟦0⟧,
           Commutator[Hn⟦0⟧, Hn⟦k1⟧]]] / (4 * k1 * k1 * (k2 - k1) * ω3)
        + Commutator[Commutator[Hn⟦k1⟧, Hn⟦0⟧],
          Commutator[Hn⟦k2 - k1⟧, Hn⟦0⟧]] / (4 * k1 * k1 * (k2 - k1) * ω3);
    ]]]];
```

In[39]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   H4S = H4S + Commutator[Hn⟦k1⟧,
        Commutator[Hn⟦0⟧, Commutator[Hn⟦0⟧, Hn⟦-k1⟧]]] * 3 / (4 * k1 * k1 * k1 * ω3)
      + Commutator[Commutator[Hn⟦-k1⟧, Hn⟦0⟧],
        Commutator[Hn⟦k1⟧, Hn⟦0⟧]] / (4 * k1 * k1 * k1 * ω3);
  ]];
```

In[40]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   H4S = H4S + Commutator[Hn⟦0⟧,
        Commutator[Hn⟦0⟧, Commutator[Hn⟦0⟧, Hn⟦k1⟧]]] / (k1 * k1 * k1 * ω3);
  ]];
```

In[41]:=
```
FullSimplify[H4S]
```

Out[41]=

$$\frac{1}{48\,\omega_r^3}\, i\,(S_{1,y} S_{2,x} - S_{1,x} S_{2,y})\,(\Omega_1 - \Omega_2)\Big(\omega_{12}[-2]^3 + 6\,\omega_{12}[-2]^2\,\omega_{12}[-1] + 12\,\omega_{12}[-2]\,\omega_{12}[-1]^2 + 8\,\omega_{12}[-1]^3 - 6\,\omega_{12}[-2]^2\,\omega_{12}[1] - 48\,\omega_{12}[-2]\,\omega_{12}[-1]\,\omega_{12}[1] - 72\,\omega_{12}[-1]^2\,\omega_{12}[1] + 72\,\omega_{12}[-1]\,\omega_{12}[1]^2 - 8\,\omega_{12}[1]^3 + 6\,\Omega_1^2\,(\omega_{12}[-2] + 8\,\omega_{12}[-1] - 8\,\omega_{12}[1] - \omega_{12}[2]) - 12\,\Omega_1\,\Omega_2\,(\omega_{12}[-2] + 8\,\omega_{12}[-1] - 8\,\omega_{12}[1] - \omega_{12}[2]) + 6\,\Omega_2^2\,(\omega_{12}[-2] + 8\,\omega_{12}[-1] - 8\,\omega_{12}[1] - \omega_{12}[2]) - 3\,(\omega_{12}[-2] - 2\,\omega_{12}[1])\,(3\,\omega_{12}[-2] + 8\,\omega_{12}[-1] - 2\,\omega_{12}[1])\,\omega_{12}[2] + 3\,(3\,\omega_{12}[-2] + 2\,\omega_{12}[-1] - 2\,\omega_{12}[1])\,\omega_{12}[2]^2 - \omega_{12}[2]^3\Big)$$

Compare the integral and commutator form of the first four orders of AHT

In[42]:=
```
FullSimplify[H1S - H1]
```
Out[42]=
```
0
```

In[43]:=
```
FullSimplify[H2S - H2]
```
Out[43]=
```
0
```

In[44]:=
```
FullSimplify[H3S - H3]
```
Out[44]=
```
0
```

In[45]:=
```
FullSimplify[H4S - H4]
```
Out[45]=
```
0
```

AHT Calculation for a dipolar-coupled three-spin system with chemical shifts

Set up the time-dependent Hamiltonian

In[1]:=
```
Commutator[A_, B_] := (A).(B) - (B).(A)
```

In[2]:=
```
Sz = {{1/2, 0}, {0, -1/2}};
Se = {{1, 0}, {0, 1}};
Sx = {{0, 1/2}, {1/2, 0}};
Sy = {{0, -I/2}, {I/2, 0}};
See = KroneckerProduct[Se, Se, Se];
S1z = KroneckerProduct[Sz, Se, Se]
S2z = KroneckerProduct[Se, Sz, Se];
S3z = KroneckerProduct[Se, Se, Sz];
S12 = 2 KroneckerProduct[Sz, Sz, Se] -
  KroneckerProduct[Sx, Sx, Se] - KroneckerProduct[Sy, Sy, Se]
S13 = 2 KroneckerProduct[Sz, Se, Sz] -
   KroneckerProduct[Sx, Se, Sx] - KroneckerProduct[Sy, Se, Sy];
```

Out[7]=

$$\left\{\left\{\frac{1}{2}, 0, 0, 0, 0, 0, 0, 0\right\}, \left\{0, \frac{1}{2}, 0, 0, 0, 0, 0, 0\right\}, \left\{0, 0, \frac{1}{2}, 0, 0, 0, 0, 0\right\}, \left\{0, 0, 0, \frac{1}{2}, 0, 0, 0, 0\right\}, \left\{0, 0, 0, 0, -\frac{1}{2}, 0, 0, 0\right\}, \left\{0, 0, 0, 0, 0, -\frac{1}{2}, 0, 0\right\}, \left\{0, 0, 0, 0, 0, 0, -\frac{1}{2}, 0\right\}, \left\{0, 0, 0, 0, 0, 0, 0, -\frac{1}{2}\right\}\right\}$$

Out[10]=

$$\left\{\left\{\frac{1}{2}, 0, 0, 0, 0, 0, 0, 0\right\}, \left\{0, \frac{1}{2}, 0, 0, 0, 0, 0, 0\right\}, \left\{0, 0, -\frac{1}{2}, 0, -\frac{1}{2}, 0, 0, 0\right\}, \left\{0, 0, 0, -\frac{1}{2}, 0, -\frac{1}{2}, 0, 0\right\}, \left\{0, 0, -\frac{1}{2}, 0, -\frac{1}{2}, 0, 0, 0\right\}, \left\{0, 0, 0, -\frac{1}{2}, 0, -\frac{1}{2}, 0, 0\right\}, \left\{0, 0, 0, 0, 0, 0, \frac{1}{2}, 0\right\}, \left\{0, 0, 0, 0, 0, 0, 0, \frac{1}{2}\right\}\right\}$$

In[12]:=
```
Ham[t_] :=
 Ω1 S1z + Ω2 S2z + Ω3 S3z + Sum[ω12[n] Exp[I n ωr t] S12 + ω13[n] Exp[I n ωr t] S13, {n, {-2, -1, 1, 2}}]
```

In[13]:=
```
Ham[t1]
```

Out[13]=

$$\left\{\left\{\frac{\Omega_1}{2} + \frac{\Omega_2}{2} + \frac{\Omega_3}{2} + \frac{1}{2} e^{-2 i\, t1\, \omega_r}\, \omega_{12}[-2] + \frac{1}{2} e^{-i\, t1\, \omega_r}\, \omega_{12}[-1] + \frac{1}{2} e^{i\, t1\, \omega_r}\, \omega_{12}[1] + \frac{1}{2} e^{2 i\, t1\, \omega_r}\, \omega_{12}[2] + \frac{1}{2} e^{-2 i\, t1\, \omega_r}\, \omega_{13}[-2] + \frac{1}{2} e^{-i\, t1\, \omega_r}\, \omega_{13}[-1] + \frac{1}{2} e^{i\, t1\, \omega_r}\, \omega_{13}[1] + \frac{1}{2} e^{2 i\, t1\, \omega_r}\, \omega_{13}[2], 0, 0, 0, 0, 0, 0, 0\right\},\right.$$

$$\Big\{0,\ \frac{\Omega_1}{2}+\frac{\Omega_2}{2}-\frac{\Omega_3}{2}+\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]+\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]+\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]+\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2]-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0,\ 0,\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0,\ 0,\ 0\Big\},$$

$$\Big\{0,\ 0,\ \frac{\Omega_1}{2}-\frac{\Omega_2}{2}+\frac{\Omega_3}{2}-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2]+\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]+\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]+\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]+\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0,\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2],\ 0,\ 0,\ 0\Big\},$$

$$\Big\{0,\ 0,\ 0,\ \frac{\Omega_1}{2}-\frac{\Omega_2}{2}-\frac{\Omega_3}{2}-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2]-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0,\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2],\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0\Big\},$$

$$\Big\{0,\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2],\ 0,\ -\frac{\Omega_1}{2}+\frac{\Omega_2}{2}+\frac{\Omega_3}{2}-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2]-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0,\ 0,\ 0\Big\},$$

$$\Big\{0,\ 0,\ 0,\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2],\ 0,\ -\frac{\Omega_1}{2}+\frac{\Omega_2}{2}-\frac{\Omega_3}{2}-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2]+\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]+\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]+\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]+\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0,\ 0\Big\},$$

$$\Big\{0,\ 0,\ 0,\ -\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0,\ 0,\ -\frac{\Omega_1}{2}-\frac{\Omega_2}{2}+\frac{\Omega_3}{2}+\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]+\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]+\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]+\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2]-\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]-\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]-\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]-\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2],\ 0\Big\},$$

$$\Big\{0,\ 0,\ 0,\ 0,\ 0,\ 0,\ 0,\ -\frac{\Omega_1}{2}-\frac{\Omega_2}{2}-\frac{\Omega_3}{2}+\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{12}[-2]+\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{12}[-1]+\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{12}[1]+\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{12}[2]+\frac{1}{2}e^{-2 i\,t1\,\omega_r}\,\omega_{13}[-2]+\frac{1}{2}e^{-i\,t1\,\omega_r}\,\omega_{13}[-1]+\frac{1}{2}e^{i\,t1\,\omega_r}\,\omega_{13}[1]+\frac{1}{2}e^{2 i\,t1\,\omega_r}\,\omega_{13}[2]\Big\}\Big\}$$

Calculate the integral form of the first four orders of AHT

In[14]:=
```
H1 = ωr / (2 π) Integrate[Ham[t1], {t1, 0, 2 π / ωr}]
```

Out[14]=

$$\left\{\left\{\frac{1}{2}(\Omega_1+\Omega_2+\Omega_3), 0, 0, 0, 0, 0, 0, 0\right\}, \left\{0, \frac{1}{2}(\Omega_1+\Omega_2-\Omega_3), 0, 0, 0, 0, 0, 0\right\}, \left\{0, 0, \frac{1}{2}(\Omega_1-\Omega_2+\Omega_3), 0, 0, 0, 0, 0\right\}, \left\{0, 0, 0, \frac{1}{2}(\Omega_1-\Omega_2-\Omega_3), 0, 0, 0, 0\right\}, \left\{0, 0, 0, 0, \frac{1}{2}(-\Omega_1+\Omega_2+\Omega_3), 0, 0, 0\right\}, \left\{0, 0, 0, 0, 0, \frac{1}{2}(-\Omega_1+\Omega_2-\Omega_3), 0, 0\right\}, \left\{0, 0, 0, 0, 0, 0, \frac{1}{2}(-\Omega_1-\Omega_2+\Omega_3), 0\right\}, \left\{0, 0, 0, 0, 0, 0, 0, \frac{1}{2}(-\Omega_1-\Omega_2-\Omega_3)\right\}\right\}$$

In[15]:=
```
H2 = -I ωr / (4 π) Integrate[Integrate[Commutator[Ham[t2], Ham[t1]], {t1, 0, t2}], {t2, 0, 2 π / ωr}]
```

In[16]:=
```
H3 = -1 ωr / (12 π) Integrate[
   Integrate[Integrate[Commutator[Ham[t3], Commutator[Ham[t2], Ham[t1]]] + Commutator[
       Commutator[Ham[t3], Ham[t2]], Ham[t1]], {t1, 0, t2}], {t2, 0, t3}], {t3, 0, 2 π / ωr}]
```

In[17]:=
```
A1 = Commutator[Ham[t4], Commutator[Ham[t3], Commutator[Ham[t1], Ham[t2]]]];
```

In[18]:=
```
A2 = Commutator[Ham[t1], Commutator[Ham[t4], Commutator[Ham[t3], Ham[t2]]]];
```

In[19]:=
```
A3 = Commutator[Ham[t1], Commutator[Ham[t2], Commutator[Ham[t3], Ham[t4]]]];
```

In[20]:=
```
A4 = Commutator[Ham[t2], Commutator[Ham[t3], Commutator[Ham[t4], Ham[t1]]]];
```

In[21]:=
```
AA = Simplify[A1 + A2 + A3 + A4];
```

In[22]:=
```
H4 = I ωr / (24 π) Integrate[
   Integrate[Integrate[Integrate[AA, {t4, 0, t3}], {t3, 0, t2}], {t2, 0, t1}], {t1, 0, 2 π / ωr}]
```

Calculate the commutator form of the first four orders of AHT

In[23]:=
```
HamC = Ham[t] //.
   {Exp[-2 I t ωr] → xr^-2, Exp[-1 I t ωr] → xr^-1, Exp[1 I t ωr] → xr^1, Exp[2 I t ωr] → xr^2};
```

In[24]:=
```
Fcoeff = CoefficientList[HamC * xr^2, {xr}];
```

In[25]:=
```
Fcoeffx = Fcoeff //. {} → {0, 0, 0, 0, 0};
```

In[26]:=
```
Fcoeffx[[All, All, 1]];
```

In[27]:=
```
Hn = Table[0 See, {n, -10, 10}];
```

In[28]:=
```
For[k = -2, k ≤ 2, k = k + 1, Hn[[k]] = Fcoeffx[[All, All, k + 3]]]
```

In[29]:=
```
H1S = Hn[[0]]
```

Out[29]=

$$\left\{\left\{\frac{\Omega_1}{2}+\frac{\Omega_2}{2}+\frac{\Omega_3}{2}, 0, 0, 0, 0, 0, 0, 0\right\}, \left\{0, \frac{\Omega_1}{2}+\frac{\Omega_2}{2}-\frac{\Omega_3}{2}, 0, 0, 0, 0, 0, 0\right\}, \left\{0, 0, \frac{\Omega_1}{2}-\frac{\Omega_2}{2}+\frac{\Omega_3}{2}, 0, 0, 0, 0, 0\right\}, \left\{0, 0, 0, \frac{\Omega_1}{2}-\frac{\Omega_2}{2}-\frac{\Omega_3}{2}, 0, 0, 0, 0\right\}, \left\{0, 0, 0, 0, -\frac{\Omega_1}{2}+\frac{\Omega_2}{2}+\frac{\Omega_3}{2}, 0, 0, 0\right\}, \left\{0, 0, 0, 0, 0, -\frac{\Omega_1}{2}+\frac{\Omega_2}{2}-\frac{\Omega_3}{2}, 0, 0\right\}, \left\{0, 0, 0, 0, 0, 0, -\frac{\Omega_1}{2}-\frac{\Omega_2}{2}+\frac{\Omega_3}{2}, 0\right\}, \left\{0, 0, 0, 0, 0, 0, 0, -\frac{\Omega_1}{2}-\frac{\Omega_2}{2}-\frac{\Omega_3}{2}\right\}\right\}$$

In[30]:=
```
H2S = 0;
For[k = -2, k ≤ 2, k = k + 1,
 If[k ≠ 0,
   H2S = H2S + 1 / 2 * Commutator[Hn[[k]], Hn[[-k]]] / (k * ω_r);
   H2S = H2S + Commutator[Hn[[0]], Hn[[k]]] / (k * ω_r);
  ];
]
```

```
In[32]:= H3S = 0;
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 If[k1 ≠ 0,
  H3S = H3S + 2 / 3 * Commutator[Hn⟦k1⟧, Commutator[Hn⟦0⟧, Hn⟦-k1⟧]] / (k1 * ωr) ^ 2;
 ]
]
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
  If[k1 ≠ 0 && k2 ≠ 0 && Abs[k1 - k2] ≤ 2,
   H3S = H3S + 1 / 3 * Commutator[Hn⟦k1⟧, Commutator[Hn⟦k2 - k1⟧, Hn⟦-k2⟧]] / (k1 * k2 * ωr * ωr);
  ]
 ]
]
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
  If[k1 ≠ 0 && k2 ≠ 0,
   H3S = H3S + 1 / 2 * Commutator[Hn⟦k2⟧, Commutator[Hn⟦-k1⟧, Hn⟦k1⟧]] / (k1 * k2 * ωr * ωr);
  ]
 ]
]
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
 For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
  If[k2 ≠ 0 && k2 ≠ -k1,
   H3S = H3S + Commutator[Hn⟦k1⟧, Commutator[Hn⟦k2⟧, Hn⟦0⟧]] / ((k1 + k2) * k2 * ωr * ωr);
  ]
 ]
]
```

In[37]:=
```
ω3 = ωr * ωr * ωr;
H4S = 0;
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 && k1 + k2 ≠ 0,
     For[k3 = -2, k3 ≤ 2, k3 = k3 + 1,
      If[k3 ≠ 0 && k3 + k2 + k1 ≠ 0,
       H4S = H4S +
          Commutator[Commutator[Hn[[k1]], Hn[[k2]]], Commutator[Hn[[k3]], Hn[[-k1 - k2 - k3]]]] / (24 * (
              k1 + k2 + k3) * (k1 + k2) * k1 * ω3)
         + Commutator[Hn[[k1]],
            Commutator[Hn[[k2]], Commutator[Hn[[k3]], Hn[[-k1 - k2 - k3]]]]] / (24 * k1 * k2 * k3 * ω3)
         + Commutator[Hn[[-k1 - k2 - k3]], Commutator[Hn[[k3]], Commutator[Hn[[k1]], Hn[[k2]]]]] /
          (6 * k1 * (k1 + k2) * (k1 + k2 + k3) * ω3);
      ]]]]]];
```

In[40]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 && k1 + k2 ≠ 0,
     For[k3 = -6, k3 ≤ 6, k3 = k3 + 1,
      If[k3 ≠ 0 && k3 - k2 - k1 ≠ 0,
       H4S = H4S + Commutator[Hn[[0]], Commutator[Hn[[k1]], Commutator[Hn[[k2]], Hn[[k3 - k2 - k1]]]]] *
          (2 * k2 - k1) / (6 * k1 * k2 * k3 * (k1 + k2) * ω3)
         + Commutator[Hn[[k3 - k2 - k1]], Commutator[Hn[[0]], Commutator[Hn[[k1]], Hn[[k2]]]]] /
          (4 * (k3 - k2 - k1) * (k1 + k2) * k2 * ω3)
         + Commutator[Commutator[Hn[[k2]], Hn[[k1]]],
            Commutator[Hn[[k3 - k2 - k1]], Hn[[0]]]] / (4 * k2 * (k1 + k2) * (k3 - k1 - k2) * ω3)
         + Commutator[Hn[[k1]], Commutator[Hn[[k3 - k1 - k2]], Commutator[Hn[[0]], Hn[[k2]]]]] /
          (6 * k1 * (k3 - k2 - k1) * k2 * ω3);
      ]]]]]];
```

In[41]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 ,
     For[k3 = -2, k3 ≤ 2, k3 = k3 + 1,
      If[k3 ≠ 0,
       H4S = H4S + Commutator[Hn[[k3]],
            Commutator[Hn[[k1]], Commutator[Hn[[-k1 - k2]], Hn[[k2]]]]] / (3 * k1 * k2 * k3 * ω3);
      ]]]]]];
```

In[42]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 ,
     For[k3 = -4, k3 ≤ 4, k3 = k3 + 1,
      If[k3 ≠ 0 && k3 - k2 ≠ 0,
       H4S = H4S + Commutator[Hn[[k3 - k2]],
            Commutator[Hn[[k2]], Commutator[Hn[[k1]], Hn[[-k1]]]]] / (4 * (k3 - k2) * k2 * k1 * ω3)
         + Commutator[Commutator[Hn[[k1]], Hn[[-k1]]],
            Commutator[Hn[[k2]], Hn[[k3 - k2]]]] / (4 * k1 * k2 * k3 * ω3);
      ]]]]]];
```

In[43]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 ,
     H4S = H4S + Commutator[Hn[[k1]],
          Commutator[Hn[[-k1]], Commutator[Hn[[-k2]], Hn[[k2]]]]] * 3 / (8 * k2 * k1 * k1 * ω3);
    ]]]];
```

In[44]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 && k1 + k2 ≠ 0,
     H4S = H4S + Commutator[Hn[[k1]],
          Commutator[Hn[[0]], Commutator[Hn[[k2]], Hn[[-k1 - k2]]]]] / (2 * k1 * k1 * k2 * ω3)
        + Commutator[Hn[[k1]], Commutator[Hn[[-k1 - k2]], Commutator[Hn[[0]], Hn[[k2]]]]] *
         (2 * k1 + k2) / (6 * k1 * k2 * k2 * (k1 + k2) * ω3)
        + Commutator[Commutator[Hn[[-k1 - k2]], Hn[[0]]],
          Commutator[Hn[[k1]], Hn[[k2]]]] / (3 * k1 * (k1 + k2) * (k1 + k2) * ω3);
    ]]]];
```

In[45]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 ,
     H4S = H4S + Commutator[Hn[[0]], Commutator[Hn[[k1]], Commutator[Hn[[k2]], Hn[[-k1]]]]] *
         (6 * k1 + k2) / (12 * k1 * k1 * k2 * k2 * ω3)
        +
        Commutator[Commutator[Hn[[k1]], Hn[[-k1]]], Commutator[Hn[[k2]], Hn[[0]]]] / (2 * k1 * k2 * k2 * ω3)
        +
        Commutator[Hn[[k2]], Commutator[Hn[[k1]], Commutator[Hn[[-k1]], Hn[[0]]]]] / (6 * k2 * k1 * k1 * ω3)
        + Commutator[Hn[[k1]],
          Commutator[Hn[[k2]], Commutator[Hn[[-k1]], Hn[[0]]]]] / (6 * k2 * k1 * k1 * ω3);
    ]]]];
```

In[46]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -2, k2 ≤ 2, k2 = k2 + 1,
    If[k2 ≠ 0 ,
     H4S = H4S +
        Commutator[Hn[[k1]], Commutator[Hn[[0]], Commutator[Hn[[0]], Hn[[k2]]]]] / (4 * k2 * k2 * k1 * ω3)
        +
        Commutator[Commutator[Hn[[k2]], Hn[[0]]], Commutator[Hn[[k1]], Hn[[0]]]] / (4 * k2 * k2 * k1 * ω3);
    ]]]];
```

In[47]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   For[k2 = -4, k2 ≤ 4, k2 = k2 + 1,
    If[k2 ≠ 0 && k2 - k1 ≠ 0,
     H4S = H4S + Commutator[Hn[[0]], Commutator[Hn[[k1]], Commutator[Hn[[0]], Hn[[k2 - k1]]]]] *
         (4 * k1 * k2 - 2 * k1 * k1 - k2 * k2) / (2 * k1 * (k2 - k1) * (k2 - k1) * k2 * k2 * ω3)
        + Commutator[Hn[[k2 - k1]],
          Commutator[Hn[[0]], Commutator[Hn[[0]], Hn[[k1]]]]] / (4 * k1 * k1 * (k2 - k1) * ω3)
        + Commutator[Commutator[Hn[[k1]], Hn[[0]]],
          Commutator[Hn[[k2 - k1]], Hn[[0]]]] / (4 * k1 * k1 * (k2 - k1) * ω3);
    ]]]];
```

In[48]:=
```
For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
  If[k1 ≠ 0,
   H4S = H4S +
      Commutator[Hn[[k1]], Commutator[Hn[[0]], Commutator[Hn[[0]], Hn[[-k1]]]]] * 3 / (4 * k1 * k1 * k1 * ω3)
      + Commutator[Commutator[Hn[[-k1]], Hn[[0]]], Commutator[Hn[[k1]], Hn[[0]]]] / (4 * k1 * k1 * k1 * ω3);
  ]];
```

```
In[49]:= For[k1 = -2, k1 ≤ 2, k1 = k1 + 1,
           If[k1 ≠ 0,
            H4S =
              H4S + Commutator[Hn[[0]], Commutator[Hn[[0]], Commutator[Hn[[0]], Hn[[k1]]]]] / (k1 * k1 * k1 * ω3);
           ]];
```

Compare the integral and commutator form of the first four orders of AHT

```
In[50]:= FullSimplify[H1S - H1]
Out[50]=
        {{0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}}

In[51]:= FullSimplify[H2S - H2]
Out[51]=
        {{0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}}

In[52]:= FullSimplify[H3S - H3]
Out[52]=
        {{0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}}

In[53]:= FullSimplify[H4S - H4]
Out[53]=
        {{0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0},
         {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, 0}}
```

References

[1] F. Bloch and A. Siegert. Magnetic resonance for nonrotating fields. *Phys. Rev.*, 57(6):522–527, 1940.

[2] David M. Brink and George R. Satchler. *Angular Momentum.* Clarendon Press, 1993.

[3] Michael Mehring. *Principles of High Resolution NMR in Solids.* Springer, 2 edition, 1983.

[4] Vera B. Cheng, Henry H. Suzukawa, Jr., and Max Wolfsberg. Investigations of a nonrandom numerical method for multidimensional integration. *J. Chem. Phys.*, 59(8):3992–3999, 1973.

[5] A Ponti. Simulation of magnetic resonance static powder lineshapes: A quantitative assessment of spherical codes. *Journal of Magnetic Resonance*, 138(2):288 – 297, 00 1999.

[6] SK Zaremba. Good lattice points, discrepancy, and numerical integration. *Annali di Matematica Pura ed Applicata*, 73(1):293 – 317, 00 1966.