Average Hamiltonian Theory
Magic Angle Spinning

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Outline

The Schrödinger equation

The Schrödinger eqn describes the evolution of a quantum state. It is expressed in terms of bra and ket as:

$$\frac{d\,|\psi\rangle}{dt} = -i\,\hat{\mathcal{H}}\,|\psi\rangle$$

$$\frac{d\,\langle\psi|}{dt} = (-i\,\hat{\mathcal{H}}\,|\psi\rangle)^\dagger = i\,\langle\psi|\,\hat{\mathcal{H}}$$

In NMR we usually describe the state of the ensemble of spin states via the density operator, so we need to move from $|\psi\rangle$ to

$$|\psi\rangle\,\langle\psi|$$

Liouville-von Neumann equation

Take the time derivative of $|\psi\rangle\langle\psi|$ to relate the S.e., which applies to the wave function, to an equation applicable to $\hat{\rho}$:

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

Taking the ensemble average and assuming $\mathcal{H}$ to be identical over the ensemble, we get the Liouville-von Neumann equation:

$$\frac{d\hat{\rho}}{dt} = i\;\left[\hat{\rho},\hat{\mathcal{H}}\right] = -i\;\left[\hat{\mathcal{H}},\hat{\rho}\right]$$

Propagators (1)

- A propagator $\hat{U}(t, t_0)$ describes the evolution of the quantum system between two time points, t_0 and t.
- $\hat{U}(t, t_0)$ is unitary, which means that

$$\begin{aligned}\hat{U}^{\dagger}(t, t_0) &= \hat{U}^{-1}(t, t_0) \\ &= \hat{U}(t_0, t)\end{aligned}$$

- Propagators are often expressed as complex exponential of Hamiltonians.
- A note of notation: t_a is a time point; τ always indicates a time interval, with $\tau_{ba} = t_b - t_a$ and $\tau \geq 0$

Propagators (2)

If $\hat{U}(t, t_0)$ describes the evolution from t_0 to t, then

$$|\psi(t)\rangle = \hat{U}(t, t_0)\, |\psi(t_0)\rangle \qquad \text{or}$$

Extend it to the density matrix via

$$\begin{aligned} \rho(t) &= |\psi(t)\rangle\langle\psi(t)| \\ &= \hat{U}(t, t_0)\, |\psi(t_0)\rangle\langle\psi(t_0)|\, \hat{U}^{\dagger}(t, t_0) \\ &= \hat{U}(t, t_0)\, \rho(t_0)\hat{U}^{-1}(t, t_0) \end{aligned}$$

For time independent $\hat{\mathcal{H}}$ the solution is known:

$$\hat{U}(t, t_0) = \exp\{-i\, \hat{\mathcal{H}}\, (t - t_0)\}$$

Our goal: given $\hat{\mathcal{H}} = \hat{\mathcal{H}}(t)$, find the propagator to evaluate

$$\rho(t) = \hat{U}(t, t_0)\rho(t_0)\hat{U}^{-1}(t, t_0)$$

L.v.N equation in terms of propagators

Start from the S.eq.

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

This becomes

$$\frac{d}{dt}\hat{U}(t,t_0)\psi(t_0) = = -i\,\hat{\mathcal{H}}(t)\hat{U}(t,t_0)\,|\psi(t_0)\rangle$$

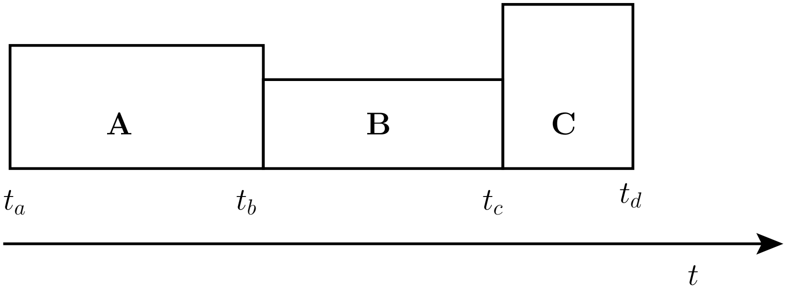
which holds for any initial $|\psi(0)\rangle$, hence we can write the L.v.N. equation directly in terms of the propagator:

$$\frac{d}{dt}\hat{U}(t,t_0) = = -i\,\hat{\mathcal{H}}(t)\hat{U}(t,t_0)$$

Evolution of the density operator

- We can describe the system evolution using propagators as
$$\rho(t) = \hat{U}(t, t_0)\rho(t_0)\hat{U}^{-1}(t, t_0)$$
- For time independent $\hat{\mathcal{H}}$ the propagator is known:
$$\hat{U}(t, t_0) = \exp\{-i\,\hat{\mathcal{H}}\,(t - t_0)\}$$
- For time dependent Hamiltonian, no closed form of $\hat{U}(t, t_0)$ is available.

Easy Case: $\hat{\mathcal{H}}$ piecewise time independent

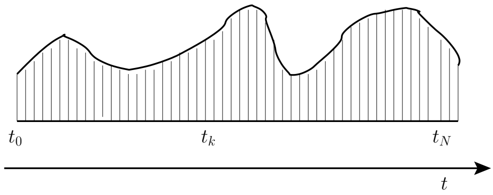


The total propagator is $\hat{U}(t_d, t_a)$, given by

$$\begin{aligned} \hat{U}(t_d, t_a) &= \hat{U}_C \hat{U}_B \hat{U}_A \\ &= \exp\{-i\hat{\mathcal{H}}_C \tau_{dc}\} \exp\{-i\hat{\mathcal{H}}_B \tau_{cb}\} \exp\{-i\hat{\mathcal{H}}_A \tau_{ba}\} \end{aligned}$$

Notice that the propagator appear in opposite order w.r.t. time plot.

Brute Force: $\hat{\mathcal{H}}(t)$ and Numerical Approach



Break up $\hat{\mathcal{H}}(t)$ into N small intervals such that $\hat{\mathcal{H}}(t_k)$ is nearly constant within each interval.
The propagator will be:

$$
\begin{aligned}
\hat{U}(t_N, t_0) &= \hat{U}(t_N, t_{N-1})\hat{U}(t_{N-1}, t_{N-2})\ldots\hat{U}(t_1, t_0) \\
&\approx \Pi_1^N \exp\{-i\hat{\mathcal{H}}(t_k)\tau_k\}
\end{aligned}
$$

This result becomes exact as $\tau_k \longrightarrow 0$

This is the approach used in many numerical programs that calculate the evolution after complicated pulse sequences.

Analytical vs numerical methods

- Numerical methods give little insight into what happens in the spin system after a pulse sequence.

- Analytical methods provide a better understanding.

- Approximations are usually necessary to obtain the analytical propagator $\hat{U}(t, t_0)$ associated with $\hat{\mathcal{H}}(t)$.

What to do, based on Hamiltonian type

We normally have one, or a mix, of the following situations:

- $\hat{\mathcal{H}}$ is small
- $\hat{\mathcal{H}}$ is not small.
  Some extra simplification steps in the interaction frame may be needed (to make it small)
- $\hat{\mathcal{H}}$ is periodic.
  Deal with the problem more easily if the observation is stroboscopic at multiples of the time period.

Interaction Frame Transformation (1)

Consider a system described by the following conditions:

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_A(t) + \hat{\mathcal{H}}_B(t)$$
$$\left[\hat{\mathcal{H}}_A(t), \hat{\mathcal{H}}_B(t)\right] \neq 0$$

where

- $\hat{\mathcal{H}}_A(t)$ big and simple to solve ($\hat{U}_A$ known)
- $\hat{\mathcal{H}}_B(t)$ small and complicated.

We want to find the propagator that solves

$$\frac{d}{dt}\hat{U} = -i\hat{\mathcal{H}}\hat{U}$$

Interaction Frame Transformation (2)

Our problem:

$$\begin{aligned} \hat{\mathcal{H}}(t) &= \hat{\mathcal{H}}_A(t) + \hat{\mathcal{H}}_B(t) \\ \frac{d}{dt}\hat{U} &= -i\hat{\mathcal{H}}\hat{U} \end{aligned}$$

We can assume without loss of generality that

$$\hat{U} = \hat{U}_A \tilde{\hat{U}}_B \qquad \longrightarrow \qquad \begin{cases} \frac{d}{dt}\hat{U}_A = -i\hat{\mathcal{H}}_A\hat{U}_A \\ \frac{d}{dt}\tilde{\hat{U}}_B = -i\tilde{\hat{\mathcal{H}}}_B\tilde{\hat{U}}_B \end{cases}$$

as $\tilde{\hat{U}}_B$ is an arbitrary unitary propagator, and the product of two unitary operators is also unitary.

It can be shown that $\tilde{\hat{U}}_B$ is associated with the Hamiltonian

$$\tilde{\hat{\mathcal{H}}}_B = \hat{U}_A^\dagger \hat{\mathcal{H}}_B \hat{U}_A$$

Interaction Frame Transformation (3)

Demonstation that $\tilde{\hat{\mathcal{H}}}_B = \hat{U}_A^\dagger \hat{\mathcal{H}}_B \hat{U}_A$:

$$\begin{aligned}
-i\hat{\mathcal{H}}\hat{U} &= \frac{d\hat{U}}{dt} \\
&= \frac{d}{dt}(\hat{U}_A \tilde{\hat{U}}_B) \\
&= \left(\frac{d}{dt}\hat{U}_A\right)\tilde{\hat{U}}_B + \hat{U}_A\left(\frac{d}{dt}\tilde{\hat{U}}_B\right) \\
-i\left(\hat{\mathcal{H}}_A + \hat{\mathcal{H}}_B\right)\hat{U}_A\tilde{\hat{U}}_B &= \left(-i\hat{\mathcal{H}}_A\hat{U}_A\right)\tilde{\hat{U}}_B + \hat{U}_A\left(-i\tilde{\hat{\mathcal{H}}}_B\tilde{\hat{U}}_B\right) \\
-i\hat{\mathcal{H}}_B\hat{U}_A\tilde{\hat{U}}_B &= -i\hat{U}_A\tilde{\hat{\mathcal{H}}}_B\tilde{\hat{U}}_B \\
\hat{U}_A^\dagger\hat{\mathcal{H}}_B\hat{U}_A\tilde{\hat{U}}_B\tilde{\hat{U}}_B^\dagger &= \hat{U}_A^\dagger\hat{U}_A\,\tilde{\hat{\mathcal{H}}}_B\tilde{\hat{U}}_B\tilde{\hat{U}}_B^\dagger \\
\hat{U}_A^\dagger\hat{\mathcal{H}}_B\hat{U}_A &= \tilde{\hat{\mathcal{H}}}_B
\end{aligned}$$

Interaction Frame Transformation (4)

- A careful look at $\hat{\mathcal{H}}$ and separation of the A and B terms is essential for an efficient semplification of the problem.
- Even though we may not be able to solve the L.v.N. equation for $\tilde{\hat{\mathcal{H}}}_B$:
  - If lucky, $\tilde{\hat{\mathcal{H}}}_B$ has become time independent.
  - $\tilde{\hat{\mathcal{H}}}_B$ is much smaller than the initial Hamiltonian, so further approximations may be applied.

Average Hamiltonian Theory - numerical approach

Any time dependent sequence can be decomposed as product of terms for which $\hat{\mathcal{H}}(t_k)$ is nearly constant:

$$\hat{U}(t_N, t_0) \approx e^{-i\hat{\mathcal{H}}(t_N)\tau} e^{-i\hat{\mathcal{H}}(t_{N-1})\tau} \dots e^{-i\hat{\mathcal{H}}(t_1)\tau}$$

It is possible to define a unitary transformation over the total $T = t_N - t_0$ interval as

$$\exp\{-i\bar{\hat{\mathcal{H}}}T\}$$

where $\bar{\hat{\mathcal{H}}}$ is the time independent average (or effective) Hamiltonian over that interval. It could for instance be obtained by diagonalising the total propagator $\hat{U}(t_N, t_0)$ and taking the log of its eigenvalues.

Average Hamiltonian Theory - BCH expansion

Given the same propagator $\hat{U}(t_N, t_0)$, instead of a numerical approach we can use approximate methods to obtain $\bar{\hat{\mathcal{H}}}$:

$$\hat{U}(t_N, t_0) \approx e^{-i\hat{\mathcal{H}}(t_N)\tau} e^{-i\hat{\mathcal{H}}(t_{N-1})\tau} \dots e^{-i\hat{\mathcal{H}}(t_1)\tau}$$

By applying many times the Baker-Campbell-Hausdorff relation

$$e^B e^A = e^{B+A+\frac{1}{2}[B,A]+\frac{1}{12}([B,[B,A]]+[[B,A],A])+\dots}$$

one can re-write it for the propagators as a series where terms with the same power of τ are collected together.

Average Hamiltonian Theory (1)

Apply the BCH equation to the propagator product with just two terms:

$$\begin{aligned} e^{-i\bar{\hat{\mathcal{H}}}2\tau} &= e^{-i\hat{\mathcal{H}}_2\tau}e^{-i\hat{\mathcal{H}}_1\tau} \\ &= e^{-i(\hat{\mathcal{H}}_1+\hat{\mathcal{H}}_2)\tau+\frac{1}{2}[\hat{\mathcal{H}}_1,\hat{\mathcal{H}}_2](i\tau)^2+\frac{1}{12}\left([\hat{\mathcal{H}}_2,[\hat{\mathcal{H}}_2,\hat{\mathcal{H}}_1]]+[\hat{\mathcal{H}}_2,[\hat{\mathcal{H}}_1,\hat{\mathcal{H}}_1]]\right)\tau^3+\ldots} \end{aligned}$$

The average Hamiltonian can be obtained from this, with different orders associated with different powers of τ

$$\begin{aligned} \tau^1 &\longrightarrow (\hat{\mathcal{H}}_1+\hat{\mathcal{H}}_2) \\ \tau^2 &\longrightarrow [\hat{\mathcal{H}}_1,\hat{\mathcal{H}}_2] \\ \tau^3 &\longrightarrow [\hat{\mathcal{H}}_2,[\hat{\mathcal{H}}_2,\hat{\mathcal{H}}_1]]+[\hat{\mathcal{H}}_2,[\hat{\mathcal{H}}_1,\hat{\mathcal{H}}_1]] \end{aligned}$$

Average Hamiltonian Theory (2)

Given an opetator $\hat{\mathcal{H}}(t)$, define a new time independent operator over an interval $t \in [0, T]$ through the Magnus series expansion:

$$
\begin{aligned}
\bar{\hat{\mathcal{H}}} &= \sum_{n=0}^{\infty} \bar{\mathcal{H}}^{(n)} \qquad \text{with} \\
\bar{\hat{\mathcal{H}}}^{(0)} &= 0 \\
\bar{\hat{\mathcal{H}}}^{(1)} &= \frac{1}{T} \int_0^T \mathcal{H}(t) dt \\
\bar{\hat{\mathcal{H}}}^{(2)} &= \frac{1}{2iT} \int_0^T dt_2 \int_0^{t_2} \left[\mathcal{H}(t_2), \mathcal{H}(t_1)\right] dt_1 \\
\bar{\hat{\mathcal{H}}}^{(3)} &= -\frac{1}{6T} \int_0^T dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} \Big\{ [\mathcal{H}(t_3), [\mathcal{H}(t_2), \mathcal{H}(t_1)]] \\
&\qquad + [[\mathcal{H}(t_3), \mathcal{H}(t_2)], \mathcal{H}(t_1)] \Big\} dt_1
\end{aligned}
$$

Convergence Criteria for AHT

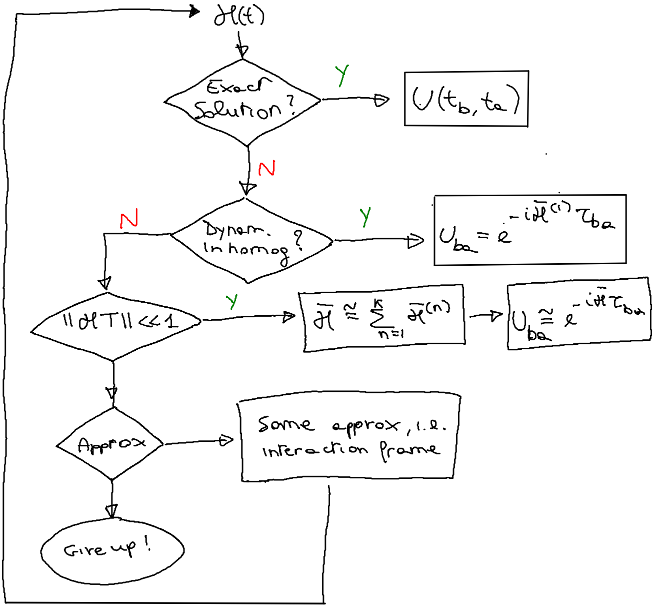
1. The Magnus series converges if $||\hat{\mathcal{H}}T|| \ll 1$.
2. AHT provides the approximate propagator *only* for time $t = NT$, if $\mathcal{H}$ has period T, with
$$\hat{U}(NT, 0) = \exp\{-i\bar{\hat{\mathcal{H}}}\, NT\}$$
3. No predictions can be made, on the basis of AHT, for what happens in between.

Note: given the difficulties in evaluating terms with $\bar{\hat{\mathcal{H}}}^{(n>2)}$, only use this approach in cases of fast convergence.

Some interesting cases for AHT

- Dynamically Inhomogeneous Hamiltonian: if
$$\left[\hat{\mathcal{H}}(t), \hat{\mathcal{H}}(t')\right] = 0 \quad \forall t, t' \in T$$
then
$$\bar{\hat{\mathcal{H}}}^{(n)} = 0 \quad \forall n > 1$$
- Antisymmetric Hamiltonian: if
$$\hat{\mathcal{H}}(t) = -\hat{\mathcal{H}}(-t)$$
then
$$\bar{\hat{\mathcal{H}}} = 0$$
- Symmetric Hamiltonian: if
$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}(-t)$$
then
$$\begin{aligned} \bar{\hat{\mathcal{H}}}^{(2n)} &= 0 \\ \bar{\hat{\mathcal{H}}} &= \sum_n \bar{\hat{\mathcal{H}}}^{(2n+1)} \end{aligned}$$

Flow diagram for AHT



Secular truncation - the tensor view

The NMR Hamiltonian can be expressed in spin tensors, which are irreducible spherical tensor operators (ISTOs).

One of the standard definition of ISTOs is due to Racah and states that the set T_{LM} constitutes an ISTO if

$$
\begin{aligned}
\left[\hat{J}_{\pm}, \hat{T}_{LM}\right] &= \sqrt{(L \mp M)(L \pm M + 1)}\,\hat{T}_{L,M\pm 1} \\
\left[\hat{J}_{z}, \hat{T}_{LM}\right] &= M\hat{T}_{LM}
\end{aligned}
$$

The high field truncation, i.e. the retention of the part of the Hamiltonian that commutes with $\hat{J}_z$, follows from it.

AHT & Secular truncation (1)

Let $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1$ where $\hat{\mathcal{H}}_0$ is the Zeeman term and $\hat{\mathcal{H}}_1$ is a spin interaction. In the IF of $\hat{\mathcal{H}}_0$, we have

$$\tilde{\hat{\mathcal{H}}}_1(t) = \hat{U}_0^{-1}(t,0)\hat{\mathcal{H}}_1\hat{U}_0(t,0)$$

Expand $\hat{\mathcal{H}}_1(t)$ in terms of a basis set made up of a complete set of suitable ISTOs, $\{\hat{Q}_k\}$

$$\begin{aligned}
\hat{\mathcal{H}}_1 &= \sum_k a_k \hat{Q}_k \\
\tilde{\hat{\mathcal{H}}}_1(t) &= \sum_k a_k \hat{U}_0^{-1}(t,0)\hat{Q}_k\hat{U}_0(t,0) \\
&= \sum_k a_k e^{-in_k\omega_0 t}\hat{Q}_k \qquad \textit{using} \\
\hat{R}_z(\alpha)\hat{T}_{\lambda\mu}\hat{R}_z(-\alpha) &= \hat{T}_{\lambda\mu}e^{-i\mu\alpha}
\end{aligned}$$

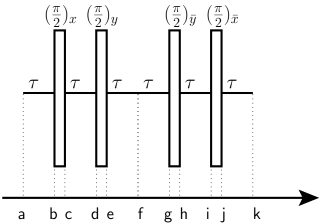
AHT & Secular truncation (2)

The first order average Hamiltonian for it over time T is

$$
\begin{aligned}
\bar{\tilde{\hat{\mathcal{H}}}}_1^{(1)} &= \frac{1}{T}\int_0^T \tilde{\hat{\mathcal{H}}}_1(t)dt \\
&= \frac{1}{T}\int_0^T \sum_k a_k e^{-in_k\omega_0 t}\hat{Q}_k dt \\
&= \frac{1}{T}\sum_k a_k\hat{Q}_k \int_0^T e^{-in_k\omega_0 t}dt \\
&= \frac{1}{T}\sum_k a_{k_0}\hat{Q}_{k_0}
\end{aligned}
$$

hence the first order average Hamiltonian over a Larmor period contains only rank 0 tensors.

WAHUHA and AHT (1)



Take 2 spins 1/2 system, no CS or J

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{rf}(t) + \omega_{DD}(3\hat{I}_{jz}\hat{I}_{kz} - \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k)$$

Assume infinitely short pulses so that the internal $\hat{\mathcal{H}}$ is neglected during the pulse.

AHT can not be applied because $||\hat{\mathcal{H}}T|| > 1$. Choose $\hat{\mathcal{H}}_A = \hat{\mathcal{H}}_{rf}(t)$

$$\hat{\mathcal{H}}_{rf}(t) = \begin{cases} 0 & t \in \text{other} \\ \omega_{\text{nut}}^I \hat{I}_x & [b, c) \\ \omega_{\text{nut}}^I \hat{I}_y & [d, e) \\ -\omega_{\text{nut}}^I \hat{I}_y & [g, h) \\ -\omega_{\text{nut}}^I \hat{I}_x & [i, j) \end{cases} \qquad \hat{U}_A(t, a) = \begin{cases} \mathbb{I} & [a, b) \\ e^{-i\frac{\pi}{2}\hat{I}_x} & [c, d) \\ e^{-i\frac{\pi}{2}\hat{I}_y} e^{-i\frac{\pi}{2}\hat{I}_x} & [e, g) \\ e^{-i\frac{\pi}{2}\hat{I}_x} & [h, i) \\ \mathbb{I} & [j, k) \end{cases}$$

WAHUHA (2)

To simplify, use the notation

$$\hat{\mathcal{H}}_{mm} = \omega_{_{DD}}(3\hat{I}_{jm}\hat{I}_{km} - \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k)$$

Calculate the transformed $\tilde{\mathcal{H}}_B$ using

$$\hat{\mathcal{H}}_B = \hat{\mathcal{H}}_{DD} = \hat{\mathcal{H}}_{zz}$$

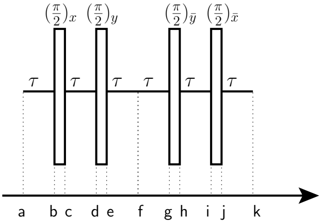
and the definition

$$\tilde{\hat{\mathcal{H}}}_B(t) = \hat{U}_A(t,a)^{\dagger}\hat{\mathcal{H}}_B\hat{U}_A(t,a)$$

For instance, in the interval $t \in [c, d)$, the interaction frame propagator is

$$e^{i\frac{\pi}{2}\hat{I}_x}\hat{\mathcal{H}}_{zz}e^{-i\frac{\pi}{2}\hat{I}_x} = \hat{\mathcal{H}}_{yy}$$

WAHUHA (3)



$$\tilde{\hat{\mathcal{H}}}_B(t) = \begin{cases} \hat{\mathcal{H}}_{zz} & t \in [a, b) \\ \hat{\mathcal{H}}_{yy} & t \in [c, d) \\ \hat{\mathcal{H}}_{xx} & t \in [e, g) \\ \hat{\mathcal{H}}_{yy} & t \in [h, i) \\ \hat{\mathcal{H}}_{zz} & t \in [j, k) \end{cases}$$

Both $\bar{\tilde{\mathcal{H}}}_B^{(1)} = 0$ and $\bar{\tilde{\hat{\mathcal{H}}}}_B^{(2)} = 0$ (symmetric $\hat{\mathcal{H}}$), because

$$\hat{\mathcal{H}}_{xx} + \hat{\mathcal{H}}_{yy} + \hat{\mathcal{H}}_{zz} = 0$$

Is $||\tilde{\hat{\mathcal{H}}}_B T|| \approx ||\tilde{\hat{\mathcal{H}}}_B 6\tau|| \ll 1$?

It depends on the timing: experimentally, it is important to have both short τ and strong pulses.

Hamiltonian & Secular truncation

$$\hat{\mathcal{H}} = \sum_{\Lambda} \hat{\mathcal{H}}^{\Lambda}$$

For any given interaction

$$\begin{aligned} \hat{\mathcal{H}}^{\Lambda} &= c^{\Lambda} \sum_{k=0}^{2} \left\langle \hat{A}^{\Lambda(k)} \middle| \hat{T}^{\Lambda(k)} \right\rangle \\ &= c^{\Lambda} \sum_{k=0}^{2} \sum_{m=-k}^{k} (-1)^m \left[\hat{A}^{\Lambda}_{km}\right] \left[\hat{T}^{\Lambda}_{k-m}\right] \end{aligned}$$

in general, but in the high field approximation only $m = 0$ remains:

$$\hat{\mathcal{H}}^{\Lambda} = c^{\Lambda} \sum_{k=0}^{2} \left[\hat{A}^{\Lambda}_{k0}\right] \left[\hat{T}^{\Lambda}_{k0}\right]$$

Hamiltonian under sample rotation

The sample rotation induces a modulation of the space tensors as:

$$\hat{\mathcal{H}}^{\Lambda} = c^{\Lambda} \sum_{k=0}^{2} \left[\hat{A}^{\Lambda}_{k0}(t)\right]^{L} \left[\hat{T}^{\Lambda}_{k0}\right]^{L}$$

$$= c^{\Lambda} \sum_{k=0}^{2} \sum_{m=-k}^{k} \left[\hat{A}^{\Lambda}_{km}\right]^{R} D^{k}_{m0}(\Omega_{RL}(t)) \left[\hat{T}^{\Lambda}_{k0}\right]^{L}$$

If $\Omega_{RL}(t) = \{\alpha^{0}_{RL} - \omega_r t, \beta_{RL}, 0\}$ then

$$\hat{\mathcal{H}}^{\Lambda} = c^{\Lambda} \sum_{k=0}^{2} \sum_{m=-k}^{k} \left[\hat{A}^{\Lambda}_{km}\right]^{R} e^{-im(\alpha^{0}_{RL} - \omega_r t)} d^{k}_{m0}(\beta_{RL}) \left[\hat{T}^{\Lambda}_{k0}\right]^{L}$$

MAS & angle definitions

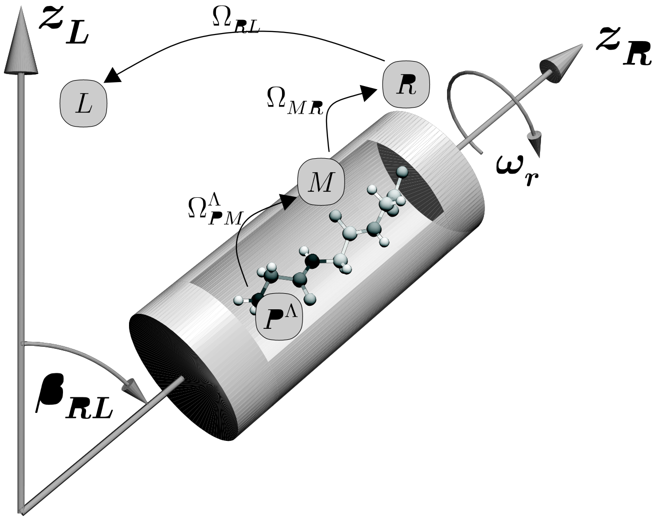


Figure from Andreas Brinkmann

Magic Angle Spinning

What happens at the magic angle, $\beta_{RL} = \arccos(1/\sqrt{3})$?

If we neglect the antisymmetric spin interactions, then

$$\begin{aligned} \hat{\mathcal{H}}^{\Lambda} &= c^{\Lambda} \left[\hat{A}^{\Lambda}_{00}\right]^{R} \left[\hat{T}^{\Lambda}_{00}\right] + \\ &\quad + c^{\Lambda} \sum_{m=-2}^{2} \left[\hat{A}^{\Lambda}_{2m}\right]^{R} e^{-im(\alpha^{0}_{RL} - \omega_r t)} d^{2}_{m0}(\beta_{RL}) \left[\hat{T}^{\Lambda}_{20}\right] \end{aligned}$$

The anisotropic interactions and the time dependence are still there.

MAS does not fully remove the anisotropic interactions, just the $m = 0$ component of rank 2 space tensors !

MAS and Average Hamiltonian Theory (1)

The Hamiltonian $\mathcal{H}^{\Lambda}$ for a spinning solid in high field is:

$$\hat{\mathcal{H}}^{\Lambda}(t) = c^{\Lambda} \left\{ \hat{A}^{\Lambda}_{iso}\, \hat{T}^{\Lambda}_{00} + \sum_{m=-2}^{2} \left[\hat{A}^{\Lambda}_{2m} \right]^{R} e^{-im(\alpha_{RL} - \omega_r t)}\, d^{2}_{m0}(\beta_{RL})\, \hat{T}^{\Lambda}_{20} \right\}$$

The first order average Hamiltonian will be

$$\begin{aligned} \bar{\hat{\mathcal{H}}}^{(1)} &= \frac{1}{\tau_r} \int_0^{\tau_r} \sum_{\Lambda} \hat{\mathcal{H}}^{\Lambda}(t) dt \\ &= \sum_{\Lambda} c^{\Lambda} \left\{ \hat{A}^{\Lambda}_{iso}\, \hat{T}^{\Lambda}_{00} + \left[\hat{A}^{\Lambda}_{20} \right]^{R} d^{2}_{00}(\beta_{RL})\, \hat{T}^{\Lambda}_{20} \right\} \\ &= \hat{\mathcal{H}}^{\mathrm{iso}} + \sum_{\Lambda} c^{\Lambda} \left[\hat{A}^{\Lambda}_{20} \right]^{R} d^{2}_{00}(\beta_{RL})\, \hat{T}^{\Lambda}_{20} \end{aligned}$$

MAS and Average Hamiltonian Theory (2)

So up to first order:

$$\bar{\hat{\mathcal{H}}}^{(1)} = \hat{\mathcal{H}}^{\text{iso}} + \sum_{\Lambda} c^{\Lambda} \left[\hat{A}^{\Lambda}_{20}\right]^{R} d^{2}_{00}(\beta_{RL})\, \hat{T}^{\Lambda}_{20}$$

and at the magic angle

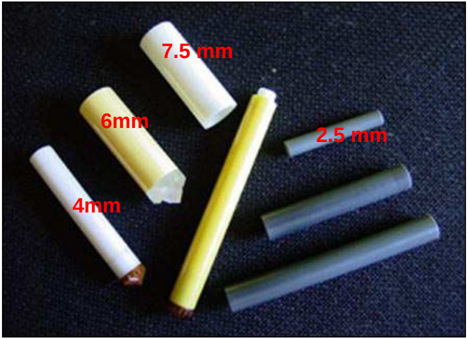
$$\bar{\hat{\mathcal{H}}}^{(1)} = \hat{\mathcal{H}}^{\text{iso}}$$

It is not straightforward to understand how AHT works because many terms do not satisfy $||\hat{\mathcal{H}}T|| \ll 1$.

A small period T (typically $T = \tau_r$ for a spinning sample) improves convergence.

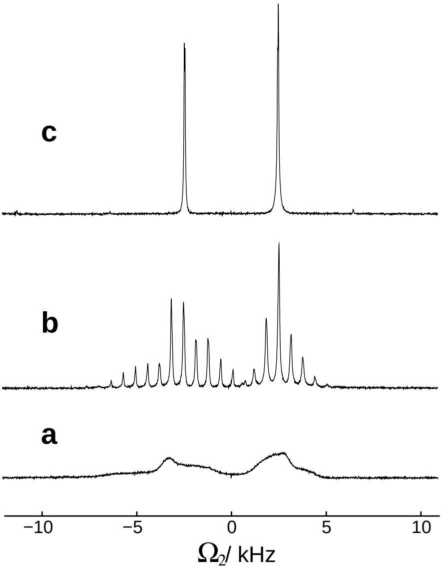
NMR Rotors

NMR rotors come in a variety of sizes. The smaller the rotor, the faster the maximum spinning frequency.



The fastest MAS probes reach speeds in excess of 100 kHz and are made by Jeol, who defeated the previous record help by Ago Samoson.

MAS and Spinning Sidebands for Glycine



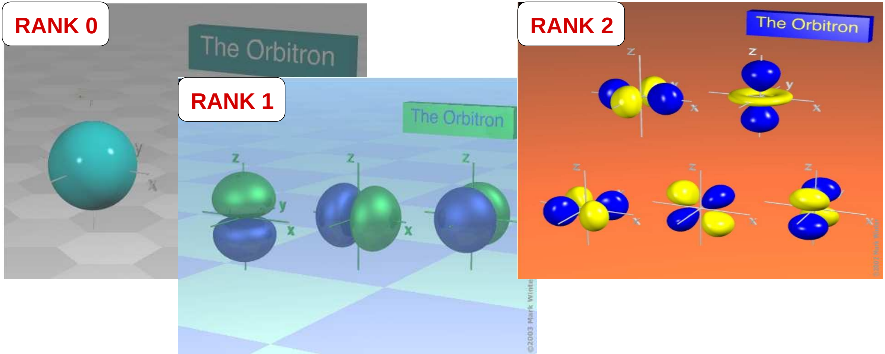
Spinning sidebands appear in (b), using conditions for which the internal $\mathcal{H}$ does not satisfy the AHT convergence condition.

Taking the CSA to be the largest interaction, we should fulfil
$||\omega^{CSA} T|| \ll 1 \longrightarrow \omega^{CSA} \ll \omega_r$

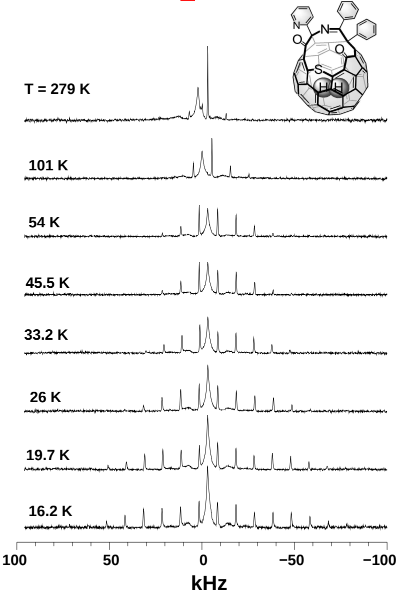
We get narrow lines because $\mathcal{H}^{CSA}$ is inhomogeneous.

Classification of spin interactions

Interaction $\mathcal{H}_{lm\lambda\mu}$	Space Rank l	Space Component m	Spin Rank λ	Spin Component μ
Iso J	0	0	0	0
Iso CS	0	0	1	-1,0,1
CSA	2	-2,-1,1,2	1	-1,0,1
DD	2	-2,-1,1,2	2	-2,-1,0,1,2



MAS of H_2 in an open fullerene

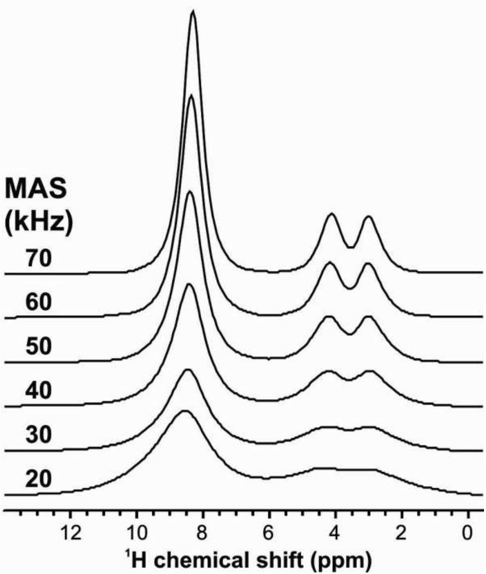


The DD coupling is T dependent.

Despite the formidable size of ω_{DD} at low T, MAS provides many narrow peaks due to the inhomogeneous nature of $\hat{\mathcal{H}}_{DD}$ for this particular sample.

This is generally not true in ^{1}H spectroscopy

MAS and ^{1}H spectrum for Glycine

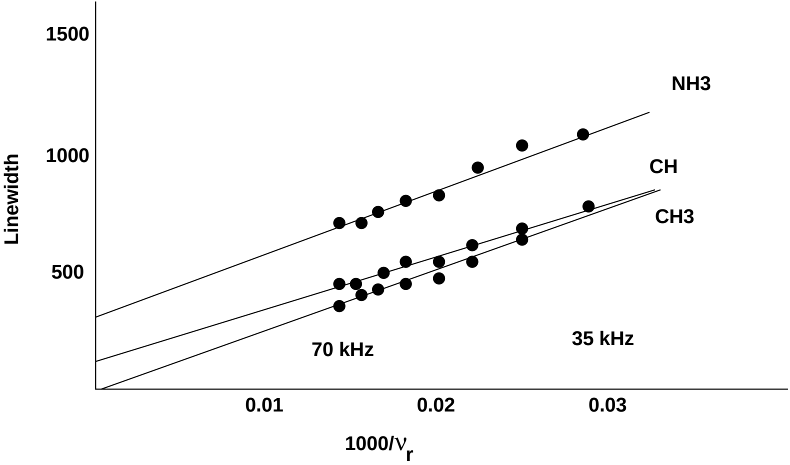


The ^{1}H signals are very broad, due to the very strong & homogeneous ^{1}H-^{1}H interactions.

AHT convergence is slow.

Image taken from http://nmr900.ca/testspectra_e.html

Alanine Proton Linewidth as function of ω_r



Much tougher case, MAS struggles to suppress the homogeneous $^1H - ^1H$ interactions even for situation in which $\omega_r > \omega_{DD}$

Figure from *Topics Curr. Chem.*, **246**, 15-31 (2005)

Conclusions

- AHT & transformation to IF can help to put problems in a form which may be analytically tractable
- Check if the Magnus series is expected to converge
- When in doubt, it is worth a try: nobody believed that MAS would be useful before it was proved to be useful
- A good balance between analytical calculations, numerical simulations and experiments, when possible, are the way to a good understanding

Selected Reading

- R. R. Ernst, G. Bodenhausen and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford, (1988).
- E. R. Andrew, A. Bradbury and R. G. Eades, *Nature* **183**, 1802–1803 (1959).
- I. J. Lowe, *Phys. Rev. Lett.* **2**, 285–287 (1959).
- M. M. Maricq and J. S. Waugh, *J. Chem. Phys.* **70**, 3300–3316 (1979).
- J. S. Waugh, L. M. Huber and U. Haeberlen, *Phys. Rev. Lett.* **20**, 180–182 (1968).
- U. Haeberlen and J. S. Waugh, *Phys. Rev.* **175**, 453–467 (1968).

... plus standard textbooks.