



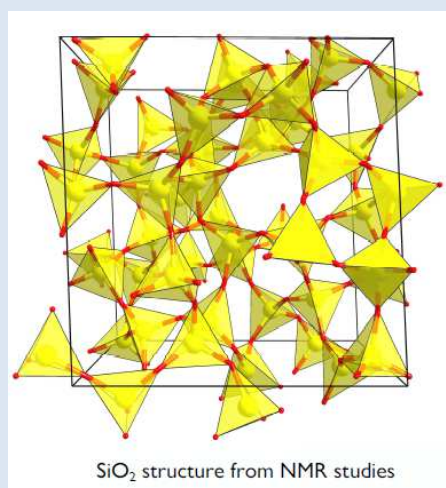
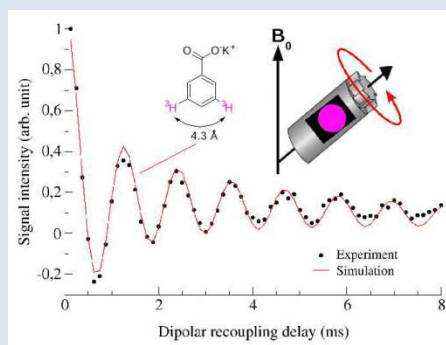
Experiment and Modelling in Structural NMR

November 28th – December 2nd 2011
INSTN – CEA Saclay, France

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Formalism and Interactions
in NMR

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Article available at <http://www.epj-conferences.org> or <http://dx.doi.org/10.1051/epjconf/20123001002>

Formalism and interactions in NMR

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Abstract. In this lecture, a fast overview of the formalism used in Nuclear Magnetic Resonance is provided, with a stress on the density matrix approach. Its equivalence to the classical derivation for particular spin systems is shown. The different interactions which are usually encountered are introduced. Finally, the case of randomly time-dependent interactions inducing relaxation is addressed.

1 Overview of the presentation

Nuclear Magnetic Resonance has a theory which is well established and very well validated. The aim of this lecture was to provide a fast introduction to this theory, more detailed and in-depth descriptions can be found in several reference books [1, 2, 5, 4, 3, 6, 7]. The presentation is organized in such a way. First, after introducing the nuclear spin, elements are provided explaining why quantum mechanics and statistical physics are needed to properly describe the evolution of the magnetization and thus predict the result of an NMR experiment. In a second step, the density matrix operator which allows such a treatment is defined and the main theorems allowing the calculation of its value at thermal equilibrium, its time-domain evolution, its expression in a rotating frame and its reduction to the spin system are given. Two simple examples of calculations (free evolution and rf excitation) performed in this framework are given. The next section is devoted to the classical approach based on the Bloch equations. The question of sensitivity in NMR is stressed and the equivalence between this approach and the density matrix one with its limits is shown. Then, the different main interactions present in conventional NMR (chemical shift, dipolar and quadrupolar interactions, scalar coupling) are described. The aspects of truncated Hamiltonian and interaction symmetries are considered. The last section is devoted to a fast introduction to relaxation due to randomly time-dependent Hamiltonian. The master equation of relaxation is derived and the principal definitions (self and cross-relaxations, auto-correlation and cross-correlation contribution to relaxation) are given. Finally the importance and relevance of spectral density functions are discussed.

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Formalism and Interactions in NMR

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Monday 28th November 2011

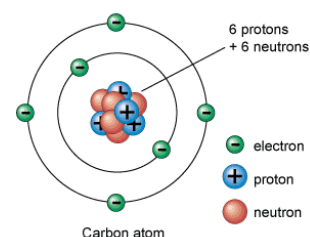


Summary of the lecture

- ① Quantum description of NMR
 - The nuclear spin
 - Properties of density matrix
 - Evolution of the density matrix
- ② Classical description
 - Key formula
 - Bloch equations
- ③ Interactions
 - Chemical shift
 - Expressions of other interactions
- ④ Principles of relaxation

Origin of the nuclear spin

- Nucleus constitution : not elementary particle
 - Protons (2 quark up, 1 quark down)
 - Neutrons (1 quarks up, 2 quarks down)
- Nuclei as atoms have quantified levels
- Nuclear spin $I \Leftrightarrow$ symmetry of the ground state
 - It is a given value (0, 1/2, 1, 3/2, 2, 5/2, ...)
 - This value is known for each isotope.
- The large difference of nucleus energy levels warranties the proportionality between the nuclear spin and the nuclear magnetic moment.



$$\vec{\mu} = \gamma \hbar \vec{I}$$

The energy of nuclear spin in a magnetic field \vec{B} is provided by the **Zeeman Hamiltonian**:

$$\mathcal{H}_Z = -\gamma \vec{I} \cdot \vec{B} \quad \mathcal{H} \text{ in } \hbar \text{ units}$$

Properties of the spin

- General properties
 - Definitions

$$[I_x, I_y] = iI_z \quad [I_y, I_z] = iI_x \quad [I_z, I_x] = iI_y$$

$$I_+ = I_x + iI_y \quad I_- = I_x - iI_y$$

$$I^2 = I_x^2 + I_y^2 + I_z^2 = I_+ I_- + I_z^2 - I_z = I_- I_+ + I_z^2 + I_z$$

$$\text{So: } [I^2, I_x] = [I^2, I_y] = [I^2, I_z] = 0$$

- Eigenvectors $|j, m_j\rangle$ with $m_j \in \{-j, -j+1, \dots, j\}$:

$$I^2 |j, m_j\rangle = j(j+1) |j, m_j\rangle; \quad I_z |j, m_j\rangle = m_j |j, m_j\rangle; \quad I_{\pm} |j, m_j\rangle \propto |j, m_j \pm 1\rangle$$

- Case of spin 1/2

- $|\alpha\rangle = |1/2, 1/2\rangle$ and $|\beta\rangle = |1/2, -1/2\rangle$:

$$I_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \quad I_x = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \quad I_y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix}$$

$$I_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad I_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

A statistical quantum description

- Need:
 - Spectroscopy \Rightarrow Quantum mechanics
 - Nuclear spin \Rightarrow Quantum mechanics
 - Wavelength \Rightarrow Statistical physics
 - Coherence \Rightarrow Quantum mechanics and statistical physics
- How :
 - Initial state given by thermodynamics
 - Density matrix description
 - Time evolution given by Liouville-Von Neumann equation
- Why is it so powerful?
 - Very weak coupling between nuclear spins and other parameters
 \Rightarrow 1st reduction of the Hilbert space
 - Most of the time, interactions between molecules are negligible
 \Rightarrow 2nd reduction of the Hilbert space
 - \Rightarrow Expectation values can analytically be computed.

Density operator expression

- Position of the problem
 - N spins 1/2 means a Hilbert space of dimension $2^N \Rightarrow$ Huge!
 - Information of a ket irrelevant: too complex and too many unknown!
 - Solution: Use of superposition of states weighted by the probability of being the representative ket.
- How? Through the density operator!
 - we search for the statistical mean of the measured values (expectation value)
 \mathcal{A} associated to an operator A
 - we call $\mathcal{P}(\psi)d\tau$ the probability of the ket $|\psi\rangle$ to describe the system
 - we call $\{|i\rangle\}$ a basis of the Hilbert space; $\mathbf{1} = \sum_i |i\rangle\langle i|$

$$\begin{aligned}
 \mathcal{A} &= \langle A \rangle = \int \mathcal{P}(\psi) \langle \psi | A | \psi \rangle d\tau \\
 &= \sum_{i,j} \int \mathcal{P}(\psi) \langle \psi | i \rangle \langle i | A | j \rangle \langle j | \psi \rangle d\tau \\
 &= \sum_{i,j} \langle i | A | j \rangle \int \mathcal{P}(\psi) \langle j | \psi \rangle \langle \psi | i \rangle d\tau \\
 &= \text{Tr}(A \cdot \rho)
 \end{aligned}$$

Density operator expression

- Position of the problem
 - N spins 1/2 means a Hilbert space of dimension $2^N \Rightarrow$ Huge!
 - Information of a ket irrelevant: too complex and too many unknown!
 - Solution: **Use of superposition of states weighted by the probability of being the representative ket.**
- How? **Through the density operator!**
- Definition
 - Expectation value: $\mathcal{A} = \text{Tr}(A \cdot \rho)$
 - where the density matrix ρ is:

$$\rho = \int \mathcal{P}(\psi) |\psi\rangle \cdot \langle\psi| d\tau$$

- If $|\psi\rangle = \sum_i a_i |i\rangle$ then $\rho_{ij} = \langle i | \rho | j \rangle = \int \mathcal{P}(\psi) a_i a_j^* d\tau = \overline{a_i a_j^*}$
- ρ_{ii} probability of finding the state $|i\rangle$ (population)
 - ρ_{ij} coherent superposition of states

Density matrix at thermal equilibrium

- General expression:
 - System at thermal equilibrium at temperature T , $\{|i\rangle\}$ a basis on which \mathcal{H}_T is diagonal: $\langle i | \mathcal{H}_T | i \rangle = E_i / \hbar$
 - No coherence between states with different energies: $\forall i \neq j, \rho_{ij} = 0$
 - The diagonal matrix elements are the state populations $p_i \propto \exp(-E_i/kT)$, thus with $\beta = \hbar/kT$

$$\rho \propto \exp(-\beta \mathcal{H}_T)$$

- Reduction to the spin system:
 - Since $\mathcal{H}_T = \mathcal{H} + \mathcal{F} + \mathcal{H}_{\mathcal{F}I}$ and there is weak coupling ($\mathcal{H}_{\mathcal{F}I}$): $\rho = \sigma \otimes \mathcal{P}$, with σ the **nuclear spin density matrix**
 - Reduced trace and high temperature approximation $E_i/kT \ll 1$:
 $\sigma = \exp -\beta \mathcal{H} \simeq \mathbf{1} - \beta \mathcal{H}$

Density matrix at thermal equilibrium

- General expression:

$$\rho \propto \exp(-\beta \mathcal{H}_T)$$

- Reduction to the spin system:

- Since $\mathcal{H}_T = \mathcal{H} + \mathcal{F} + \mathcal{H}_{\mathcal{F}I}$ and there is weak coupling ($\mathcal{H}_{\mathcal{F}I}$): $\rho = \sigma \otimes \mathcal{P}$, with σ the nuclear spin density matrix
- Reduced trace and high temperature approximation $E_i/kT \ll 1$:
 $\sigma = \exp(-\beta \mathcal{H}) \simeq \mathbf{1} - \beta \mathcal{H}$

- Final expression in a high magnetic field:

- Spin Hamiltonian expression:

$$\mathcal{H} \simeq - \sum_{\text{molecules}} \sum_{\text{spin}} \gamma B_0 I_z^k$$

- In a dilute spin system \Rightarrow average molecule

$$\sigma = \mathbf{1} + \sum_k \gamma B_0 I_z^k$$

Time-domain evolution

- Schrödinger equation:

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

- The Liouville-Von Neumann equation is obtained from the Schrödinger equation and the definition of ρ :

$$\frac{d\rho}{dt} = -i[\mathcal{H}_T, \rho]$$

- Evolution of one observable:

$$\begin{aligned} \frac{d\mathcal{A}}{dt} &= \frac{d\langle A \rangle}{dt} = \frac{d}{dt} \text{Tr}(\rho \cdot A) = \text{Tr} \left(\frac{d\rho}{dt} \cdot A \right) = \text{Tr}(-iA \cdot [\mathcal{H}_T, \rho]) \\ &= \langle -i[A, \mathcal{H}_T] \rangle \end{aligned}$$

Free evolution of the magnetization

- Key equations:
 - Initial state: $\sigma = \mathbf{1} - \sum_k \gamma B_0 I_z^k$
 - Time evolution: $\frac{d}{dt}\sigma = -i[\mathcal{H}, \sigma]$
 - Observation: $\langle A \rangle = \text{Tr}(A \cdot \sigma)$
 - Time evolution: $\frac{d}{dt}\langle A \rangle = \langle -i[A, \mathcal{H}] \rangle$
- Free evolution of $I_+ = I_x + iI_y$
 - Hamiltonian $\mathcal{H} = \omega_0 I_z$
 - Evolution of I_x : $\frac{d}{dt}\langle I_x \rangle = -i\langle [I_x, \omega_0 I_z] \rangle = -\omega_0 \langle I_y \rangle$
 - Evolution of I_y : $\frac{d}{dt}\langle I_y \rangle = -i\langle [I_y, \omega_0 I_z] \rangle = \omega_0 \langle I_x \rangle$
 - So: $\frac{d}{dt}\langle I_+ \rangle = i\omega_0 \langle I_+ \rangle \Rightarrow \langle I_+ \rangle(t) = \langle I_+ \rangle(0)e^{i\omega_0 t}$
 - **Precession around Oz at ω_0 .**

RF excitation

- Change of representations
 - Unitary transformation defined by U : $U \cdot U^\dagger = U^\dagger \cdot U = \mathbf{1}$ i.e. $U^\dagger = U^{-1}$
 - With $\frac{d}{dt}U(t) = iA(t) \cdot U(t)$ with $A(t)$ hermitian.

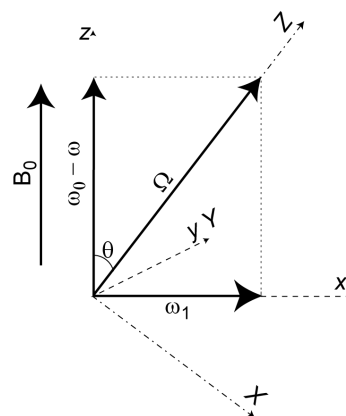
$$\begin{aligned} \frac{d\tilde{\sigma}}{dt} &= \frac{d}{dt}(U \cdot \sigma \cdot U^\dagger) = \dot{U} \cdot \sigma \cdot U^\dagger + U \cdot \frac{d\sigma}{dt} \cdot U^\dagger + U \cdot \sigma \cdot \dot{U}^\dagger \\ &= -i[\tilde{\mathcal{H}} - A(t), \tilde{\sigma}] = -i[\mathcal{H}_{\text{effective}}, \tilde{\sigma}] \end{aligned}$$

- Example: $\mathcal{H} = \omega_0 I_z + 2\omega_1 \cos \omega t I_x$

- $U(t) = \exp(i\omega I_z t)$, $A(t) = \omega I_x$
- In the interaction frame:

$$\begin{aligned} \frac{d\tilde{\sigma}}{dt} &= -i[(\omega_0 - \omega)I_z + \omega_1 I_x, \tilde{\sigma}] \\ &= -i[\Omega I_Z, \tilde{\sigma}] \end{aligned}$$

- **Precession around the tilted effective field**
- $\tan \theta = \omega_1 / (\omega_0 - \omega)$
- $\Omega = \sqrt{(\omega_0 - \omega)^2 + (\omega_1)^2}$



Simple forms

 θ pulse:

$$I_z \xrightarrow{\theta_y} I_z \cos \theta + I_x \sin \theta$$

$$I_z \xrightarrow{\theta_x} I_z \cos \theta - I_y \sin \theta$$

$$I_{x,y} \xrightarrow{\theta_{x,y}} I_{x,y}$$

$$I_x \xrightarrow{\theta_y} I_x \cos \theta - I_z \sin \theta$$

$$I_y \xrightarrow{\theta_x} I_y \cos \theta + I_z \sin \theta$$

Chemical shift:

$$I_z \xrightarrow{\omega t I_z} I_z$$

$$I_x \xrightarrow{\omega t I_z} I_x \cos \omega t + I_y \sin \omega t$$

$$I_y \xrightarrow{\omega t I_z} I_y \cos \omega t - I_x \sin \omega t$$

Scalar interactions:

	$I_{1z,2z}$	$\frac{2\pi J_{12} t I_{1z} I_{2z}}{\hbar}$	$I_{1z,2z}$
	$2I_{1z} I_{2z}$	$\frac{2\pi J_{12} t I_{1z} I_{2z}}{\hbar}$	$2I_{1z} I_{2z}$
	$2I_{1x,1y} I_{2x,2y}$	$\frac{2\pi J_{12} t I_{1z} I_{2z}}{\hbar}$	$2I_{1x,1y} I_{2x,2y}$
	I_{1x}	$\frac{2\pi J_{12} t I_{1z} I_{2z}}{\hbar}$	$I_{1x} \cos \pi J t + 2I_{1y} I_{2z} \sin \pi J t$
	I_{1y}	$\frac{2\pi J_{12} t I_{1z} I_{2z}}{\hbar}$	$I_{1y} \cos \pi J t - 2I_{1x} I_{2z} \sin \pi J t$
	$2I_{1x} I_{2z}$	$\frac{2\pi J_{12} t I_{1z} I_{2z}}{\hbar}$	$2I_{1x} I_{2z} \cos \pi J t + I_{1y} \sin \pi J t$
	$2I_{1y} I_{2z}$	$\frac{2\pi J_{12} t I_{1z} I_{2z}}{\hbar}$	$2I_{1y} I_{2z} \cos \pi J t - I_{1x} \sin \pi J t$

Magnetization of a spin 1/2

Polarization at thermal equilibrium

$$P = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \tanh \frac{\gamma \hbar B_0}{2kT} \simeq \frac{\gamma \hbar B_0}{2kT}$$

Magnetization evolution

$$\frac{d\vec{\mathcal{M}}}{dt} = \gamma \vec{\mathcal{M}} \wedge \vec{B}_0$$

Magnetization

$$\mathcal{M}_z = P \mu N \simeq \frac{\gamma^2 \hbar^2 N B_0}{4kT}$$

Detection

$$\frac{d\mathcal{M}_\perp}{dt} = \gamma B_0 \mathcal{M}_\perp = \frac{1}{4} \frac{\gamma^3 \hbar^2 B_0^2 N}{kT}$$

Signal-to-noise ratio

$$\text{Noise} \propto \sqrt{\gamma B_0}$$

$$\text{SNR} \propto N \gamma^{5/2} B_0^{3/2}$$

$$\text{With probe sensitivity: SNR} \propto N \gamma^{11/4} B_0^{7/4}$$

Equivalence to the quantum description

- Hamiltonian: $\mathcal{H} = -\gamma \vec{I} \cdot \vec{B}_0$
- Evolution:

$$\frac{d\langle \vec{\mathcal{M}} \rangle}{dt} = -i \langle [\vec{\mathcal{M}}, \mathcal{H}] \rangle = i\gamma^2 \hbar \langle [\vec{I}, \vec{I} \cdot \vec{B}_0] \rangle$$

$$\begin{aligned} \frac{d\langle \mathcal{M}_z \rangle}{dt} &= i\gamma^2 \hbar \langle [I_z, \vec{I} \cdot \vec{B}_0] \rangle \\ &= \gamma^2 \hbar (B_{0y} \langle I_x \rangle - B_{0x} \langle I_y \rangle) \\ &= \gamma^2 \hbar (\langle \vec{I} \rangle \wedge \vec{B}_0)_z \\ &= \gamma (\langle \vec{\mathcal{M}} \rangle \wedge \vec{B}_0)_z \end{aligned}$$

Bloch equations

- Assumptions:
 - Homogeneous magnetization and static magnetic field
 - **No interaction**
 - One spin species
- Expressions:

$$\begin{aligned} \frac{d\mathcal{M}_x(t)}{dt} &= -\omega_0 \mathcal{M}_y(t) - \frac{\mathcal{M}_x(t)}{T_2} \\ \frac{d\mathcal{M}_y(t)}{dt} &= \omega_0 \mathcal{M}_x(t) - \frac{\mathcal{M}_y(t)}{T_2} \\ \frac{d\mathcal{M}_z(t)}{dt} &= -\frac{\mathcal{M}_z(t) - \mathcal{M}_0}{T_1} \end{aligned}$$

- T_1 is the longitudinal self-relaxation time.
- T_2 is the transverse self-relaxation time.

Can be extended to take into account: cross-relaxation, chemical exchange, ...
but not to everything!

Origin of the chemical shift

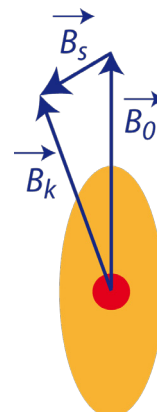
- Information on the chemical function
- Results from the induced magnetic fields (electronic spins, electronic current, ...)

$$\vec{B}_k = \vec{B}_S + \vec{B}_0$$

$$\begin{pmatrix} B_{Sx} \\ B_{Sy} \\ B_{Sz} \end{pmatrix} = - \begin{pmatrix} \sigma_{xx}^{(k)} & \sigma_{xy}^{(k)} & \sigma_{xz}^{(k)} \\ \sigma_{yx}^{(k)} & \sigma_{yy}^{(k)} & \sigma_{yz}^{(k)} \\ \sigma_{zx}^{(k)} & \sigma_{zy}^{(k)} & \sigma_{zz}^{(k)} \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$

- The Hamiltonian is computed using \vec{B}_k
- By neglecting non-secular terms:

$$\mathcal{H}_{CS}^I = \sum_k \gamma B_0 (1 - \sigma_{zz}^{(k)}) I_z^k$$



Tensorial expression of the chemical shift

- A particular molecular frame defines the principal axis system:

$$\underline{\sigma}^{(k)} = \begin{pmatrix} \sigma_{11}^{(k)} & 0 & 0 \\ 0 & \sigma_{22}^{(k)} & 0 \\ 0 & 0 & \sigma_{33}^{(k)} \end{pmatrix}$$

- Thus

$$\underline{\sigma}^{(k)} = \sigma_{\text{iso}}^{(k)} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{\sigma_{11}^{(k)} + \sigma_{22}^{(k)} - 2\sigma_{33}^{(k)}}{6} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} + \frac{\sigma_{11}^{(k)} - \sigma_{22}^{(k)}}{2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

- Isotropic chemical shift $\sigma_{\text{iso}}^{(k)} = \frac{\sigma_{11}^{(k)} + \sigma_{22}^{(k)} + \sigma_{33}^{(k)}}{3}$
- Second-rank tensorial contributions \Rightarrow averaged out by Brownian motion in liquids.

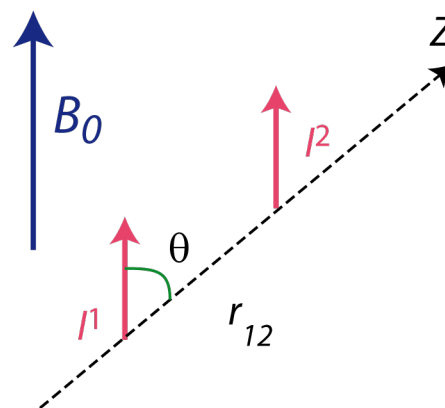
Dipolar interactions

- **Structural information (distance, angle)**
- Dipolar interaction between two nuclear spins

$$\mathcal{H}_D = \frac{\mu_0 \gamma^2 \hbar}{4\pi r_{12}^3} \left(\vec{I}^1 \cdot \vec{I}^2 - 3I_Z^1 I_Z^2 \right)$$

- Truncated dipolar interactions:

$$\mathcal{H}'_D = \frac{\mu_0 \gamma^2 \hbar}{4\pi r_{12}^3} \frac{1 - 3 \cos^2 \theta}{2} \cdot \left(2I_z^1 I_z^2 - \frac{1}{2}(I_+^1 I_-^2 + I_-^1 I_+^2) \right)$$

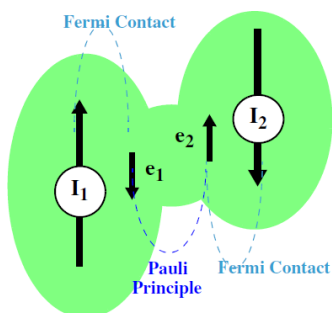


- Only second-rank tensor contribution \Rightarrow no effect on resonance frequency in liquids.

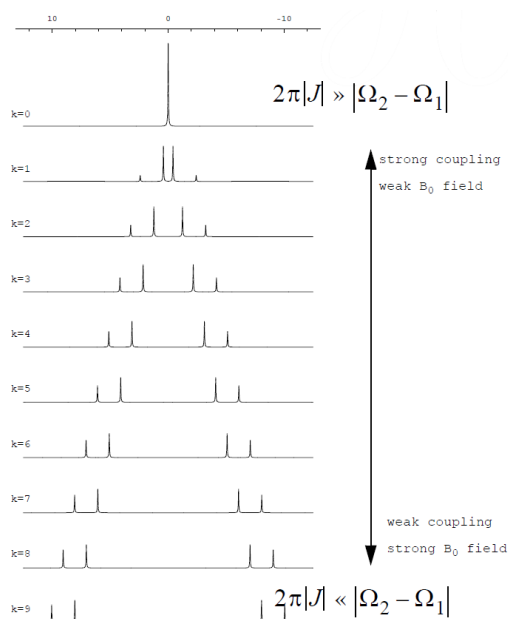
Scalar couplings

- **Information on the connectivity and on dihedral angles**
- Interactions between two nuclear spins through chemical bonds (via electrons)
- Mainly isotropic interaction

$$\mathcal{H}_J = 2\pi J \vec{I}^1 \cdot \vec{I}^2$$

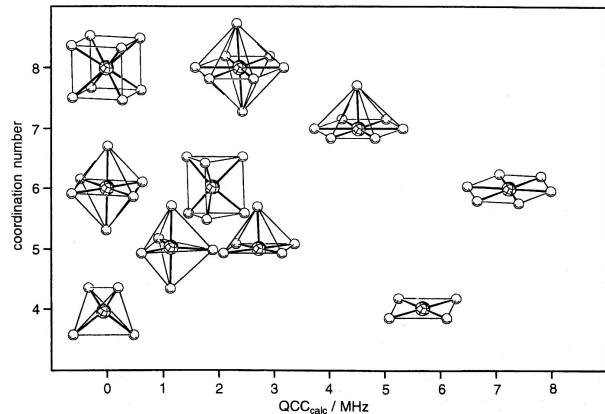


Weak coupling: $\mathcal{H}_J = 2\pi J I_z^1 I_z^2$



Quadrupolar interactions

- **Structural information**
- All nuclei of spin larger than 1/2 have a quadrupolar contribution.
- Interaction of the electric quadrupole moment (eQ) with the electric field gradient \underline{V} .
- Quadrupolar coupling
 $C_Q = (eQV_{ZZ})/h$
- Amplitude from 0 to 30MHz
 $\Rightarrow \mathcal{H} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_Q$.



C_Q values as a function of Al-site symmetry.

$$H_Q = \frac{eQV_{ZZ}}{4I(2I-1)\hbar} (3I_Z^2 - I(I+1) + \eta(I_x^2 - I_y^2)) \quad \text{with} \quad \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

Master equation of relaxation

- Hamiltonian: $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$ where $\mathcal{H}_1(t) = \sum_{\alpha} V_{\alpha} F_{\alpha}(t)$ and $\overline{F_{\alpha}(t)} = 0$
- In the interaction frame $U = e^{i\mathcal{H}_0 t}$: $\frac{d}{dt} \tilde{\sigma} = -i[\mathcal{H}_1(t), \tilde{\sigma}]$, $\tilde{V}_{\alpha}(t) = e^{i\omega_{\alpha} t} V_{\alpha}$
- Double integration and averaging:

$$\tilde{\sigma}(t) = \tilde{\sigma}(0) - i \int_0^t [\mathcal{H}_1(t'), \tilde{\sigma}(t')] dt'$$

$$\frac{d}{dt} \tilde{\sigma}(t) = -i[\mathcal{H}_1(t), \tilde{\sigma}(0)] - \int_0^t [\mathcal{H}_1(t), [\mathcal{H}_1(t'), \tilde{\sigma}(t')]] dt'$$

$$\frac{d}{dt} \overline{\tilde{\sigma}(t)} = - \int_0^t \overline{[\mathcal{H}_1(t), [\mathcal{H}_1(t'), \tilde{\sigma}(t')]]} dt'$$

- Assumptions
 - τ_c correlation time
 - Slow evolution for time short compared τ_c
 - Time t very large when compared to τ_c
 - Replacement of $\tilde{\sigma}$ by $\tilde{\sigma} - \tilde{\sigma}_{\text{eq}}$
 - $\overline{F_{\alpha}(t) F_{\beta}^*(t')}$ only depends on $|t - t'|$
 - Secular approximation

Master equation of relaxation

- Hamiltonian: $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$ where $\mathcal{H}_1(t) = \sum_{\alpha} V_{\alpha} F_{\alpha}(t)$ and $\overline{F_{\alpha}(t)} = 0$
- Double integration and averaging:

$$\frac{d}{dt} \tilde{\sigma}(t) = - \int_0^t \overline{[\tilde{\mathcal{H}}_1(t), [\tilde{\mathcal{H}}_1(t'), \tilde{\sigma}(t')]]} dt'$$

- Assumptions
- Master equation of relaxation

$$\frac{d}{dt} \tilde{\sigma}(t) = - \sum_{\alpha} [V_{\alpha}, [V_{\alpha}^{\dagger}, (\tilde{\sigma}(t) - \tilde{\sigma}_{\text{eq}})]] J_{\alpha}(\omega_{\alpha})$$

with J_{α} the spectral density:

$$J_{\alpha}(\omega) = \int_0^{\infty} \overline{F_{\alpha}(t) F_{\alpha}^*(t + \tau) e^{i\omega\tau}} d\tau$$

Key features of relaxation

- Evolution due to relaxation of one operator:

$$\frac{d}{dt} \langle \tilde{Q} \rangle(t) = - \sum_{\alpha} \left(\left\langle [[\tilde{Q}, V_{\alpha}], V_{\alpha}^{\dagger}] \right\rangle(t) - \left\langle [[\tilde{Q}, V_{\alpha}], V_{\alpha}^{\dagger}] \right\rangle_{\text{eq}} \right) J_{\alpha}(\omega_{\alpha})$$

- **Self-relaxation** and **cross-relaxation**

$$\frac{d}{dt} \langle \tilde{Q} \rangle(t) = -\lambda \langle \tilde{Q} \rangle(t) - \mu \langle \tilde{Q}' \rangle(t) + \dots$$

- **Autocorrelation twice the same interaction, cross-correlation two different**

$$\mathcal{H}_1(t) = \sum_k \mathcal{H}_1^{(k)}(t) \text{ and } \frac{d}{dt} \tilde{\sigma}(t) = - \int_0^{\infty} \overline{[\tilde{\mathcal{H}}_1(t), [\tilde{\mathcal{H}}_1(t'), \tilde{\sigma}(t') - \tilde{\sigma}_{\text{eq}}]]} dt'$$

Key features of relaxation

- Evolution due to relaxation of one operator:

$$\frac{d}{dt}\langle\tilde{Q}\rangle(t) = -\sum_{\alpha}\left(\langle[[\tilde{Q}, V_{\alpha}], V_{\alpha}^{\dagger}]\rangle(t) - \langle[[\tilde{Q}, V_{\alpha}], V_{\alpha}^{\dagger}]\rangle_{\text{eq}}\right) J_{\alpha}(\omega_{\alpha})$$

- **Self-relaxation** and **cross-relaxation**
- **Autocorrelation** twice the same interaction, **cross-correlation** two different
- **Spectral density** contains all structural and dynamic pieces of information

$$J_{\alpha}(\omega) = \int_0^{\infty} \overline{F_{\alpha}(t)F_{\alpha}^{*}(t+\tau)} e^{i\omega\tau} d\tau$$

