The Basics of NMR

A macroscopic quantum system:

Although the magnetic dipoles of near-by spins interact, the *rapid rotational diffusion* of the molecules in liquids average these interactions to zero. Hence to an excellent first-order approximation, spins in different molecules *do not interact*. It follows that if the state of the spins in the m-th molecule is $|\psi^m\rangle$, then density operator of an M molecule ensemble factorizes as follows:

$$\widehat{\Psi} = \overline{|\psi^1\psi^2\ldots\psi^M\rangle\langle\psi^1\psi^2\ldots\psi^M|}$$

$$= \overline{|\psi^1\rangle\langle\psi^1|\cdots|\psi^M\rangle\langle\psi^M|} = \overline{|\psi^1\rangle\langle\psi^1|}\ \cdots\ \overline{|\psi^M\rangle\langle\psi^M|}$$

$$= \Psi^1\Psi^2\ldots\Psi^M \approx \Psi^{\otimes M} \quad \left(\Psi \equiv M^{-1}\textstyle\sum_m \overline{|\psi^m\rangle\langle\psi^m|}\right)$$

Thus the *kinematics* is identical to that of a single molecule!

The dynamics and observables are also identical, since:

$$e^{-it\sum_m \mathbf{H}^m}\left(\Psi^{\otimes M}\right)e^{it\sum_m \mathbf{H}^m} = \left(e^{-it\mathbf{H}}\Psi e^{it\mathbf{H}}\right)^{\otimes M}$$

$$\operatorname{tr}\left(\Psi^{\otimes M}\textstyle\sum_m \sigma_\alpha^m\right) = M\operatorname{tr}(\Psi\sigma_\alpha^m)$$

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Lecture #4

The weak-coupling Hamiltonian:

The Hamiltonian of liquid-state NMR has the form:

$$\mathbf{H} = -\tfrac{1}{2}\sum_k \omega_0^k \sigma_3^k + \tfrac{\pi}{2}\sum_{k<l} J^{kl}(\sigma_1^k\sigma_1^l + \sigma_2^k\sigma_2^l + \sigma_3^k\sigma_3^l)$$

The first term is the Zeeman interaction (in rad/sec) with the external magnetic field (along z) as before; the second is the **scalar coupling** of pairs of spins across chemical bonds.

It follows from first-order perturbation theory that if $|\omega_0^k - \omega_0^l| >> \pi J^{kl} \quad \forall k, l$ (weak coupling), the scalar coupling terms may be replaced by their secular parts $\pi J^{kl}\sigma_3^k\sigma_3^l$. Now since $\mathbf{H}$ is diagonal, $\exp(-\iota t\mathbf{H})$ may be given in closed form.

Radio-frequency fields:

Given a strong RF-field on-resonance with the k-th spin,

$$\mathbf{H}_{\mathrm{RF}} = \omega_1^k(\cos(\omega_0^k t)\sigma_1^k + \sin(\omega_0^k t)\sigma_2^k) = \omega_1^k \exp(\iota\omega_0^k t\sigma_3^k)\sigma_1^k$$

with $\omega_1^k >> \pi|J^{kl}| \quad \forall l$, it follows from the Liouville-von Neumann equation that in a co-rotating frame

$$\Psi' = \exp(-\iota\omega_0^k t\sigma_3^k)\Psi\exp(\iota\omega_0^k t\sigma_3^k),$$

the (spin vector of) the spin rotates about the x' axis according to $\exp(-\iota\omega_1^k t\sigma_{1'}^k)$. Henceforth, all our transform-ations will be referred to such a *rotating frame* (w/o primes).

In-Phase & Anti-phase Coherence

The effect of scalar coupling:

The (weak) scalar coupling propagator has the form:

$$\exp(-\iota\pi J^{12} t\sigma_3^1\sigma_3^2/2) \;=\; \cos(\pi J^{12} t/2) - \iota\sin(\pi J^{12} t/2)\sigma_3^1\sigma_3^2$$

Applied to a transverse state of e.g. spin 1, this yields:

$$\exp(-\iota 2\pi J^{12} t\sigma_3^1\sigma_3^2/2)\sigma_1^1\exp(\iota 2\pi J^{12} t\sigma_3^1\sigma_3^2/2)$$

$$= \cos(\pi J^{12} t)\sigma_1^1 + \sin(\pi J^{12} t)\sigma_2^1\sigma_3^2$$

This is a rotation between **in-phase** (σ_1^1) and **anti-phase** ($\sigma_2^1\sigma_3^2$) coherence on spin 1.

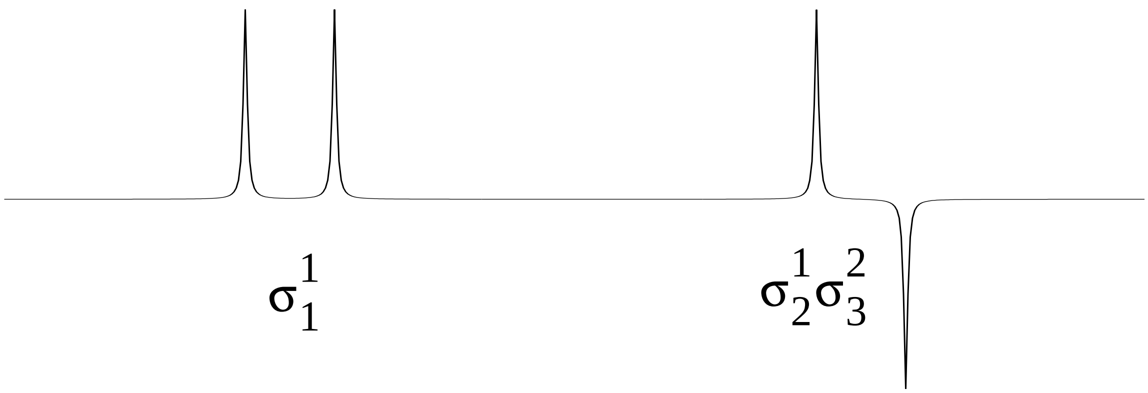
A classical interpretation is found on rotating to the z-axis, where the diagonal matrix elements in the σ_3 basis ($|0\rangle \equiv |\uparrow\rangle$, $|1\rangle \equiv |\downarrow\rangle$) are deviations from equal *populations*:

PO	$\langle 00\|PO\|00\rangle$	$\langle 10\|PO\|10\rangle$	$\langle 01\|PO\|01\rangle$	$\langle 11\|PO\|11\rangle$
σ_3^1	1	-1	1	-1
$\sigma_3^1\sigma_3^2$	1	-1	-1	1

The anti-phase population *difference* between $|0\rangle$ & $|1\rangle$ states of spin 1 is inverted in the subensemble where spin 2 is down.

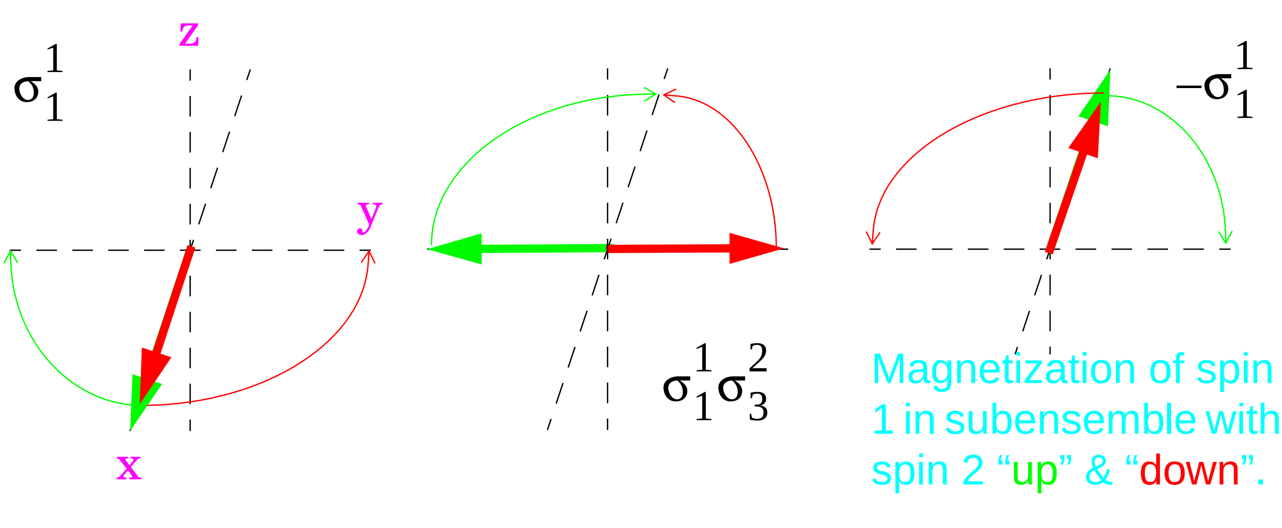
Spectra & vector diagrams:

Thus in- / anti-phase coherence corresponds to classical ensembles, characterized by these relative populations, which are *in transition* between spin 1 "up" & "down". Moreover, spin 1's magnetization (population difference) precesses at the rate $\omega_0^1/(2\pi) \pm J^{12}$ as spin 2 is "up" or "down", resp. The spectrum (real part of the Fourier transform) is,



in which the anti-phase population inversion may be seen.

The rotation of σ_1^1 into $\sigma_2^1\sigma_3^2$ may be visualized as follows:



The one-bit quantum logic gates:

The simplest logic gate is the NOT, which is a π-rotation about the x-axis combined with a phase shift,

$$\exp\left(\iota\frac{\pi}{2}(1-\sigma_1^k)\right) = \iota\left(\cos(\pi/2)-\iota\sin(\pi/2)\sigma_1^k\right) = \sigma_1^k;$$

recalling that the density operators of the basis states of the k-th spin (with a totally mixed state everywhere else) are

$$(\mathbf{1}\otimes\ldots\otimes|0\rangle\langle 0|\otimes\ldots\otimes\mathbf{1}) = \tfrac{1}{2}(1+\sigma_3^k) \equiv \mathbf{E}_+^k$$

$$(\mathbf{1}\otimes\ldots\otimes|1\rangle\langle 1|\otimes\ldots\otimes\mathbf{1}) = \tfrac{1}{2}(1-\sigma_3^k) \equiv \mathbf{E}_-^k \;,$$

we can use the anticommutivity of σ_1^k & σ_3^k to show that this NOT gate maps the $|0\rangle$ state of the k-th spin to the $|1\rangle$ state:

$$\sigma_1^k\,\mathbf{E}_+^k\sigma_1^k = \sigma_1^k\,\tfrac{1}{2}(1+\sigma_3^k)\sigma_1^k = (\sigma_1^k)^2\tfrac{1}{2}(1-\sigma_3^k) = \mathbf{E}_-^k$$

◆ Another important one-bit, but *nonboolean*, gate is the Hadamard transform HAD:

$$\exp\left(\iota\frac{\pi}{2}(1-\sqrt{2}(\sigma_1^k+\sigma_3^k))\right) = \sqrt{2}(\sigma_1^k+\sigma_3^k),$$

which can be show to map $\sigma_1^k \leftrightarrow \sigma_3^k$ & $\sigma_2^k \leftrightarrow -\sigma_2^k$. It also maps $|0\rangle \leftrightarrow (|0\rangle+|1\rangle)/\sqrt{2}$ & $|1\rangle \leftrightarrow (|0\rangle-|1\rangle)/\sqrt{2}$, and so can be used to prepare a uniform superposition over all spins as above.

The multi-bit boolean logic gates:

Interesting computations require feedback, i.e. the state of one bit must influence what happens to another, but the usual AND & OR gates are *not* reversible (only one output!).

An important two-bit gate is the **controlled-NOT**:

$$\exp\left(\iota\frac{\pi}{2}(1-\sigma_1^1)\mathbf{E}_-^2\right) = \sigma_1^1\mathbf{E}_-^2 + \mathbf{E}_+^2$$

This “c-NOT” is readily shown to flip the first spin in states where the second is down (just as we considered earlier), i.e.

$$|00\rangle \leftrightarrow |00\rangle \qquad |10\rangle \leftrightarrow |10\rangle \qquad |01\rangle \leftrightarrow |11\rangle \qquad |11\rangle \leftrightarrow |01\rangle,$$

or more compactly: $|\delta^1\delta^2\rangle \leftrightarrow |(\delta^1 + \delta^2 \bmod 2)(\delta^2)\rangle$. Thus idempotents also describe the *conditionality* of operations.

Another obvious gate is the SWAP of two bits,

$$\mathrm{p}\left(\iota\frac{\pi}{2}\Pi^{12}\right) = \Pi^{12} \equiv \frac{1}{2}\left(1 + \sigma_1^1\sigma_1^2 + \sigma_2^1\sigma_2^2 + \sigma_3^1\sigma\right.;$$

Π^{12} is also called the **particle interchange operator**.

These can be extended to N bits; e.g., the **Toffoli gate** is:

$$\exp\left(\iota\frac{\pi}{2}(1-\sigma_1^1)\mathbf{E}_-^2\mathbf{E}_-^3\right) = \sigma_1^1\mathbf{E}_-^2\mathbf{E}_-^3 + (1-\mathbf{E}_-^2\mathbf{E}_-^3)$$

The TOF alone is *universal* for boolean logic; more generally, the c-NOT and one-bit rotations *generate* all of $\mathrm{SU}(2^N)$.

NMR Implementations of Gates

Radio-frequency pulse sequences:

The NOT gate is easily implemented by a strong RF pulse, in phase with the x-axis, whose frequency range spans only the resonance of the target spin, and whose duration is sufficient to rotate it by π (note the global phase offset of ι has no effect on the density operator).

The HAD gate is similarly obtained from the pulse sequence (written in left-to-right temporal order):

$$\left[\frac{\pi}{8}\sigma_2^k\right] \to \left[\frac{\pi}{2}\sigma_1^k\right] \to \left[-\frac{\pi}{8}\sigma_2^k\right] \Leftrightarrow \exp\left(\iota\frac{\pi}{8}\sigma_2^k\right)\exp\left(-\iota\frac{\pi}{2}\sigma_1^k\right)\exp\left(-\iota\frac{\pi}{8}\sigma_2^k\right)$$

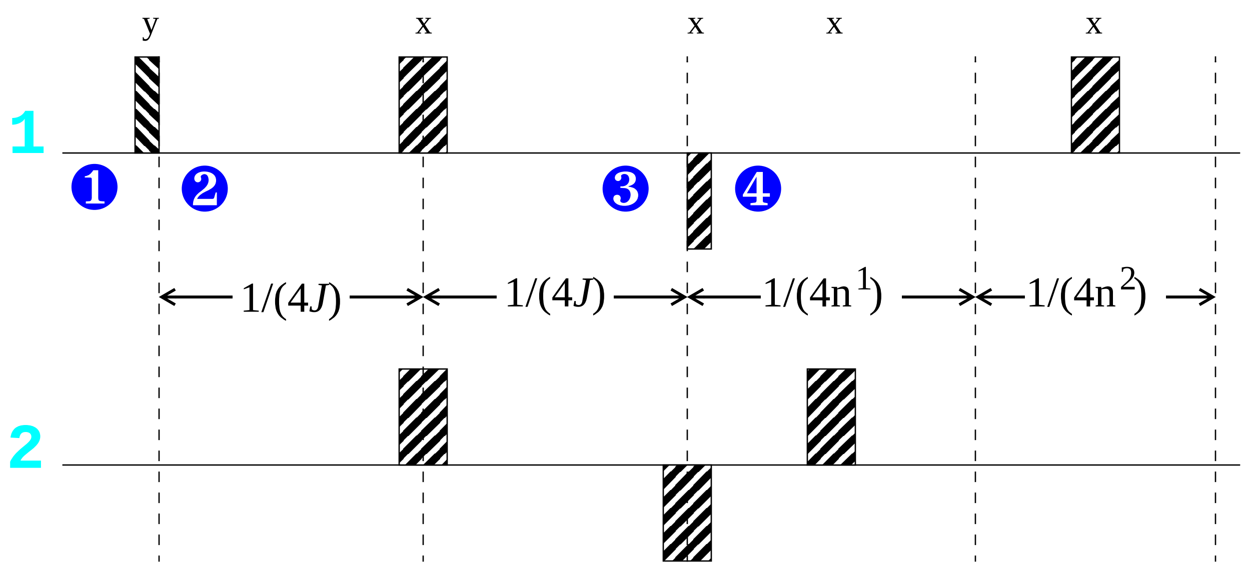
To implement the c-NOT gate, we proceed as follows:

$$\begin{aligned}\exp\left(\iota\frac{\pi}{2}(1-\sigma_1^1)\mathbf{E}_-^2\right) &= \exp\left(-\iota\frac{\pi}{4}\sigma_2^1\right)\exp\left(\iota\pi\mathbf{E}_-^1\mathbf{E}_-^2\right)\exp\left(\iota\frac{\pi}{4}\sigma_2^1\right)\\ &= \exp\left(-\iota\frac{\pi}{4}\sigma_2^1\right)\exp\left(-\iota\frac{\pi}{4}(\sigma_3^1+\sigma_3^2)\right)\exp\left(\iota\frac{\pi}{4}\sigma_3^1\sigma_3^2\right)\exp\left(\iota\frac{\pi}{4}\sigma_2^1\right)\sqrt{\iota}\\ &= \exp\left(-\iota\frac{\pi}{4}(\sigma_3^1+\sigma_3^2)\right)\exp\left(-\iota\frac{\pi}{4}\sigma_1^1\right)\exp\left(\iota\frac{\pi}{4}\sigma_3^1\sigma_3^2\right)\exp\left(\iota\frac{\pi}{4}\sigma_2^1\right)\sqrt{\iota}\end{aligned}$$

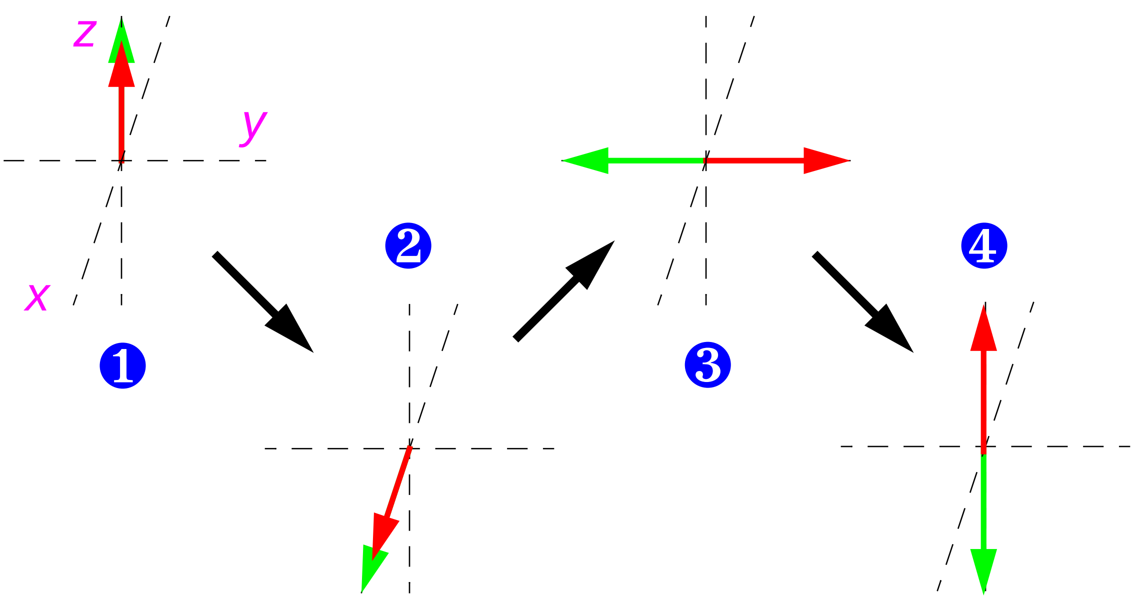
This is a $(\pi/2)$-rotation about y, a weak coupling evolution for $1/(2J^{12})$, a $(\pi/2)$-rotation about x, and a Zeeman evolution.

Vector diagram description:

- This pulse sequence may be depicted as follows:



In terms of Bloch diagrams, we have:



Caption: Here, **red** is magnetization of **1** spin in molecules where **2** spin is up, and **green** that of **1** spin where **2** down.

PSEUDO-PURE STATES

Starting from equilibrium:

Since $|2\pi J| << |\omega_0| << k_B T$, the **equilibrium state** of a homonuclear spin system (& its partition function $Q \approx 2^N$) is:

$$\Psi_{eq} = \frac{\exp(-\mathbf{H}_Z / k_B T)}{\mathrm{tr}(\exp(-\mathbf{H}_Z / k_B T))} = \frac{\exp\left(-\sum_l \omega_0^l \sigma_3^l / 2 k_B T\right)}{Q}$$

$$\approx \left(1 - \sum_l \omega_0^l \sigma_3^l / 2 k_B T\right) 2^{-N} \approx \left(1 - \frac{\omega_0 \sum_i p_i |i\rangle\langle i|}{k_B T}\right) 2^{-N}$$

Here $|0101\ldots0\rangle$ is a binary expansion of $|i\rangle$, & $p_i = h(i) - N/2$ where $h(i)$ is the **Hadamard weight** (number of 1's) of i.

The problem with Ψ_{eq} is that logical operations performed on the spins at the *microscopic* level do not effect the same operations on their *macroscopic* polarizations; for two spins:

	PO	$\langle 00 \vert PO \vert 00 \rangle$	$\langle 10 \vert PO \vert 10 \rangle$	$\langle 01 \vert PO \vert 01 \rangle$	$\langle 11 \vert PO \vert 11 \rangle$
ρ_{eq}	$\sigma_3^1 + \sigma_3^2$	1	0	0	–1
ρ'_{eq}	$\mathbf{E}_+^1 \sigma_3^2$	1	0	–1	0

Spin 1's polarization, i.e. the alternating row sum, goes to 0.

So we average yet more!

A **pseudo-pure state** is one whose density operator has exactly one nondegenerate eigenvalue, e.g.

$$\Psi_{pp} = \left(1 - \frac{\omega_0 p_0 |\mathbf{0}\rangle\langle\mathbf{0}|}{k_B T}\right) 2^{-N} \equiv (1 + \alpha\,|\mathbf{0}\rangle\langle\mathbf{0}|)\, 2^{-N}.$$

Note that the microscopic state $|\mathbf{0}\rangle = |00\ldots0\rangle$ is *canonically* associated with ρ_{pp}.

Because the identity component is unitarily *invariant*, the state $|i\rangle$ provides a *spinorial* representation of $\mathrm{SU}(2^N)$:

$$\mathbf{U}\Psi_{pp}\tilde{\mathbf{U}} = (1 + \alpha\,(\mathbf{U}|\mathbf{0}\rangle)(\langle\mathbf{0}|\tilde{\mathbf{U}}))\,2^{-N} \qquad \left(\mathbf{U} \in \mathrm{SU}(2^N)\right)$$

Similarly, because the identity component does *not* contribute to the magnetization (population differences), the ensemble average expectation value of the observables is proportional to their ordinary *expectation values*:

$$\frac{1}{2}\mathrm{tr}(\Psi_{pp}\sigma_1^k) = \left(\mathrm{tr}(\sigma_1^k) + \alpha\,\mathrm{tr}(\sigma_1^k|\mathbf{0}\rangle\langle\mathbf{0}|)\right)2^{-N-1} = \frac{\alpha}{2^{N+1}}\langle\mathbf{0}|\sigma_1^k|\mathbf{0}\rangle$$

Since their eigenstructures differ, Ψ_{pp} must be prepared from Ψ_{eq} by a *nonunitary* process, e.g. by averaging the popu-lations over all permutations of the states $|i\rangle\langle i|$ $(i > 0)$ (more efficient methods exist, which rely upon magnetic gradients).