

From Spin Hamiltonian to Spectra

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This document is now online: DOI [10.3247/SL4Nmr13.005](https://doi.org/10.3247/SL4Nmr13.005)

Note:

Some of the historic preamble, and some of the mathematical machinery apply also to electron spin. But the core of this tutorial is concerned with

Nuclear Magnetic Resonance (NMR)

and not with the equally important

Electron Spin Resonance (ESR)

A Tutorial

*at the Joint Conference of the German, Italian and Slovenian Magnetic Resonance Societies
(FGMR-GIDRM-SLONMR) Chiemsee, Germany, 9-12 Sep 2013*

A. History of Magnetic Spin Resonance

Spin Hamiltonian ? What is « **spin** » ??

Good questions!

It all started with electrons,
before kind of overflowing into nuclides

A mini-chronicle of electron spin

- 1897: **Pieter Zeeman** finds that magnetic field broadens spectral lines
- 1921: **Arthur H. Compton** advocates axial electrons to explain magnetism
- Atoms have nearly twice the expected number of spectral lines
- In the Wilson cloud chamber, electron trajectories have strange “kinks”
- 1925: **Ralph Kronig** suggests that electron has an angular momentum (spin)
- **Wolfgang Pauli** tells him it is a foolish idea and poor Ralph desists !
- Later in 1925: **George E. Uhlenbeck** & **Samuel A. Goudsmit** submit a paper to *Naturwissenschaften*, also claiming that electron has a spin
- They show it to the great **Hendrik A. Lorentz** who deems it impossible !
- They urge the Editor to *please* withdraw the paper, but it is too late !
- Fortunately, further investigations by many physicists prove them correct. The paper becomes a cornerstone of modern physics !
- 1927: a converted **Wolfgang Pauli** builds the best formal model of spin
- Later: **Paul A.M. Dirac**, the theoretician, says that “... *a particle with a spin of half a quantum is really simpler than a particle with no spin at all ...*”
- In other words: ***what's all the fuss about, isn't it trivial to start with ?***

The dawn of nuclear spins

- In 1922, the experiment of **Otto Stern** and **Walter Gerlach** confirms the quantization of the *directions* of an angular momentum (*spin is unknown!*)
- In 1927, **David M. Dennison** studies the thermodynamics of the hydrogen molecule and notes that proton should have spin $\frac{1}{2}$ to explain the results
- Still in 1927, **T.E. Phipps** and **J.B. Taylor** reproduce the Stern-Gerlach experiment with protons (instead of the more complex silver atoms)
- The idea that nuclei may possess a spin is generally accepted in 1927-28. So is the realization that proton has spin $\frac{1}{2}$
- In 1937 **Isidor Isaac Rabi** adds the RF (gyrating magnetic field) to the Stern-Gerlach setup and the **molecular rays method** is born
- In 1938 the group of **Isidor I. Rabi** exploits resonance to *precisely* measure nuclear magnetic moments (*converting field strength to frequency!*)

Magnetic Resonance is born,

albeit not in bulk matter.

By 1945, many nuclear moments are quite precisely known, including that of neutron (L.W. Alvarez, F. Bloch, 1940)

In 1938 it was known *for sure** that:

There are particles of many kinds
and all the particles of each kind are exactly alike,
and some kinds have a permanent
half-integer spin
and thus an immutable
angular momentum \mathbf{M} ,
always associated with a
magnetic moment $\boldsymbol{\mu}$,
and all these quantities are vectors.

$$\mathbf{M} = \hbar\mathbf{S} \quad \boldsymbol{\mu} = \gamma\mathbf{M} \quad \hbar \dots \text{Planck constant, } \gamma \dots \text{gyromagnetic ratio}$$

Plus, all particles obey the exclusion principle!

* Well, at least that is what we still believe, and it still takes an awful lot of Faith.
It covers about half of Quantum Physics

The quest for MR in condensed phases

- 1936: The idea is already around. **W.Heitler** & **E.Teller** estimate nuclear spin-lattice relaxation rates which might pre-condition its viability!
- 1936: **C.J.Görter** describes a resonant apparatus for NMR in bulk matter
- 1936: **C.J.Görter** reports a failure ! They used to do *that* then ...
- 1937: **B.G.Lasarew** & **L.W.Schubnikow** detect nuclear contribution to the susceptibility of liquid H₂. This is an early non-resonant measurement!
- 1940: **F.Bloch** & **A.Siegert** publish a theoretical study of an MR effect which will be confirmed experimentally only many years later.
- 1941: **W.E.Lamb** estimates internal diamagnetic fields induced by electron shells: theoretical introduction of chemical shifts and their predictions!
- 1941: **Evgenij Zavoisky** reportedly sees NMR signals in bulk matter but, since they are badly reproducible, dismisses the finding!
- 1942: **C.J.Görter** & **L.J.F.Broer** report another failure! The guys are plain unlucky: without knowing it, they pick up only samples with extremely long relaxation times like LiF, LiCl, KF (looking for ¹⁹F and ⁷Li).

Had they used whisky, or even *just* water, the Nobel was their's!

First clear signals from bulk matter

1944, in Kazan (ex Soviet Union, now Tatarstan):

Evgenij K.Zavoisky discovers ESR (same as EPR and EMR)

1945, December 15, at Harvard University, Massachusetts:

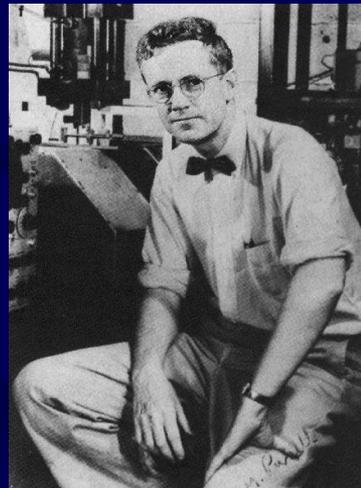
Edward M.Purcell, H.C.Torrey and **Robert V.Pound** detect NMR

1945, December 23, at Stanford University, California:

Felix Bloch, W.W.Hansen, Martin E.Packard detect NMR



Evgenij Zavoijsky



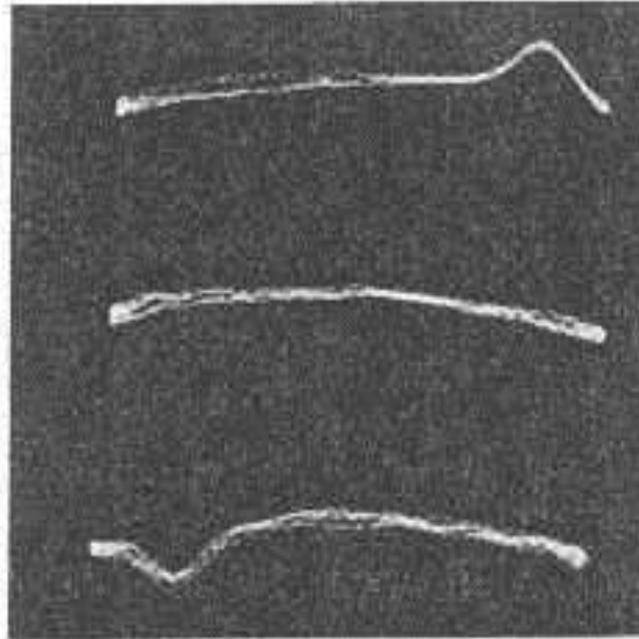
Edward Purcell



Felix Bloch

How did the first signals look?

1945 ...

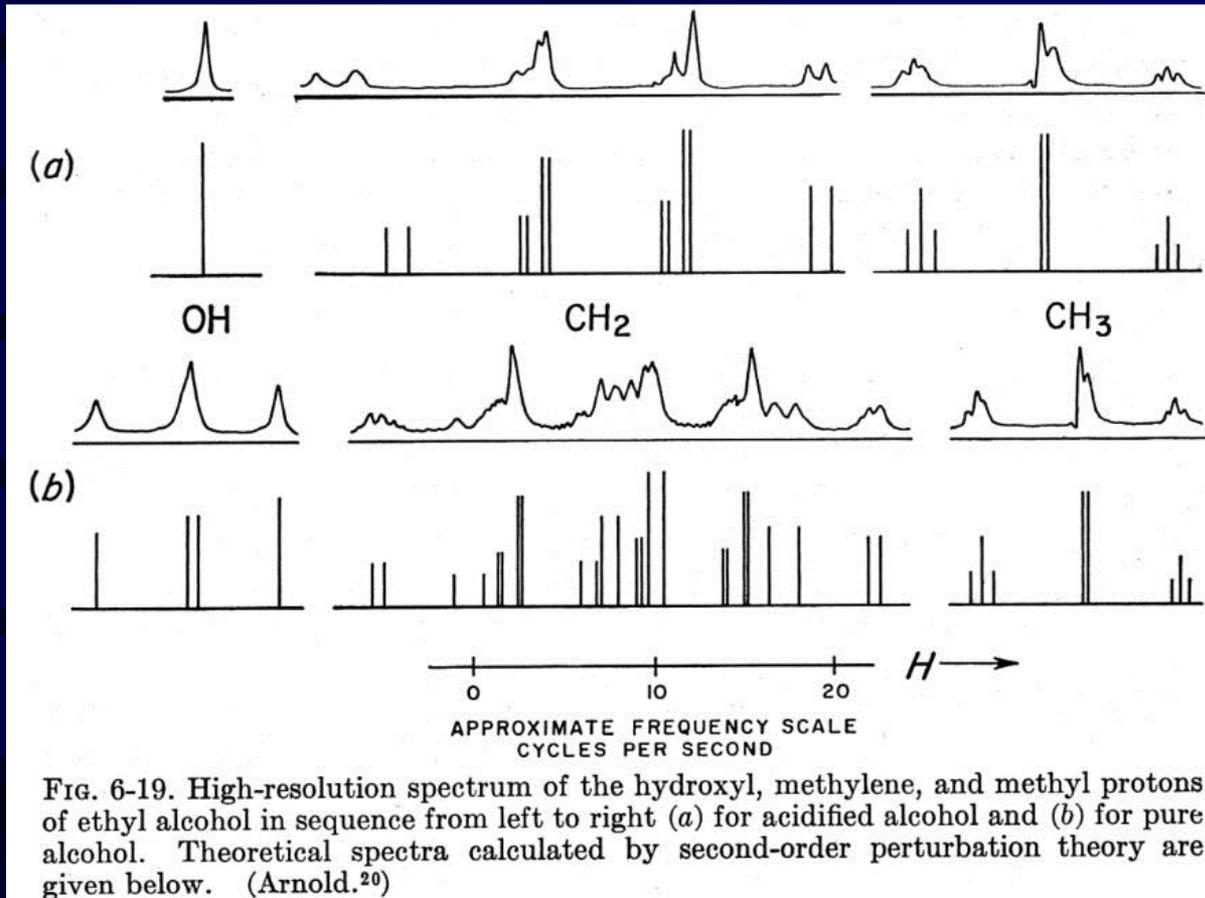


A photographic record of the first NMR signal (doped water protons)

The three traces differ by the RF phase difference between the transmitter and the receiver (0° , 90° , and 180°)

From: Felix Bloch, Nuclear Induction, Phys.Rev. 69, 127 (1946)

Rapid emergence of chemical applications



... 1955

30 MHz spectrum – but the linewidth was only about 0.2 Hz:
Typically, it is ! MUCH ! worse today, in 2013, shame on us!

First commercial instruments

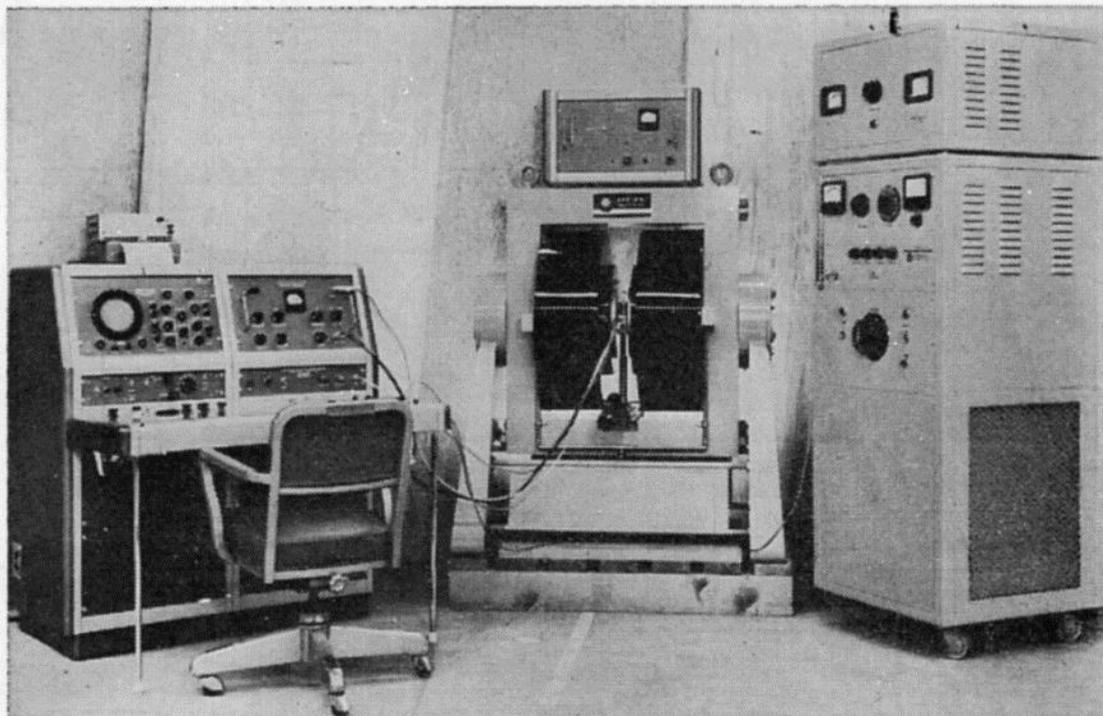


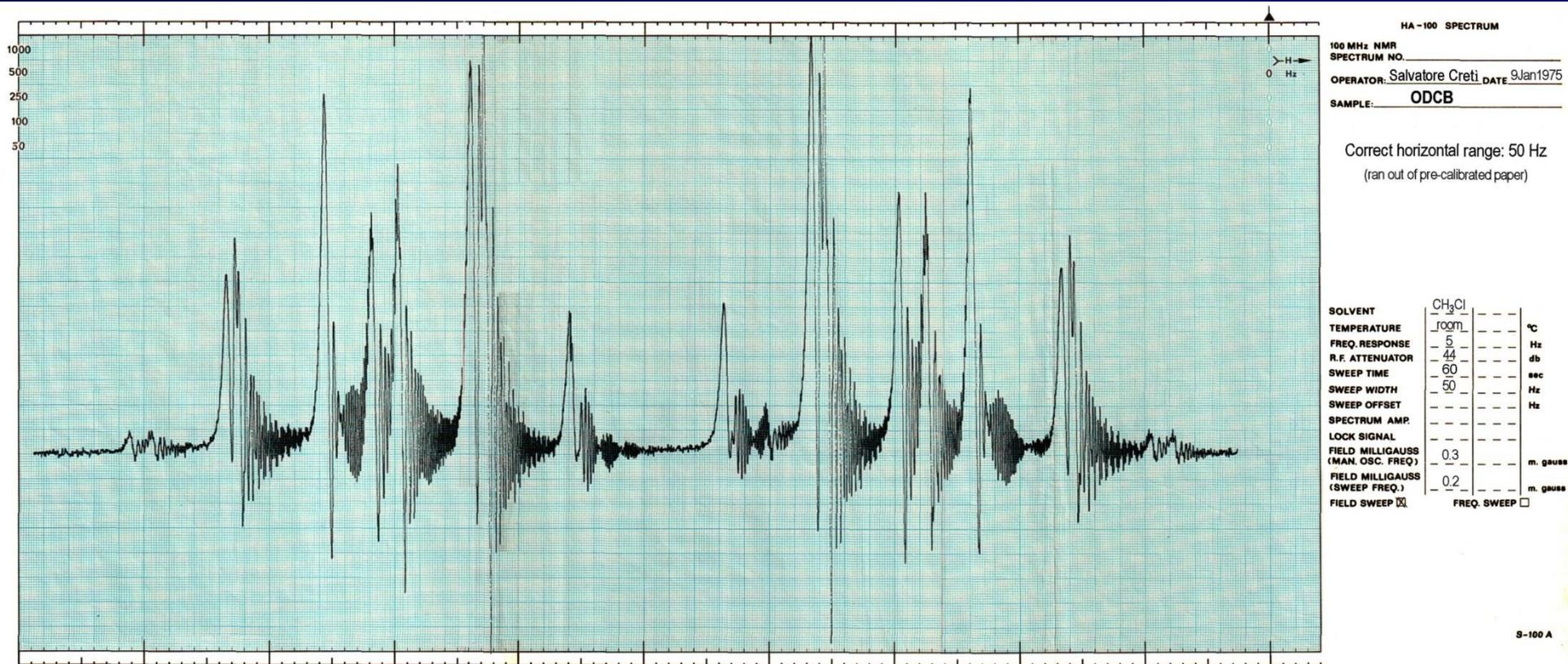
FIG. 4-8. Photograph of the Varian High Resolution Spectrometer with 12-in. magnet. (Courtesy of Varian Associates.)

The Varian T30

NMR spectrometers in existence, . Russell Varian, who had studied MR, which Bloch did—receiving a very broad patent. Russell and his brother then took a license to the NMR patent, which they transferred to Varian Associates when they founded the company in April 1948. The first commercial NMR spectrometer was built by Varian Associates in 1950–51. The first three high-resolution NMR spectrometers commercialized were delivered to Humble Oil, Shell Development Corporation, and the Du Pont experimental station. These were operating by 1952.

(Eric von Hippel: *The Sources of Innovation*, Oxford University Press, 1988)

The CW era: 1945 to ~1970 ... to today



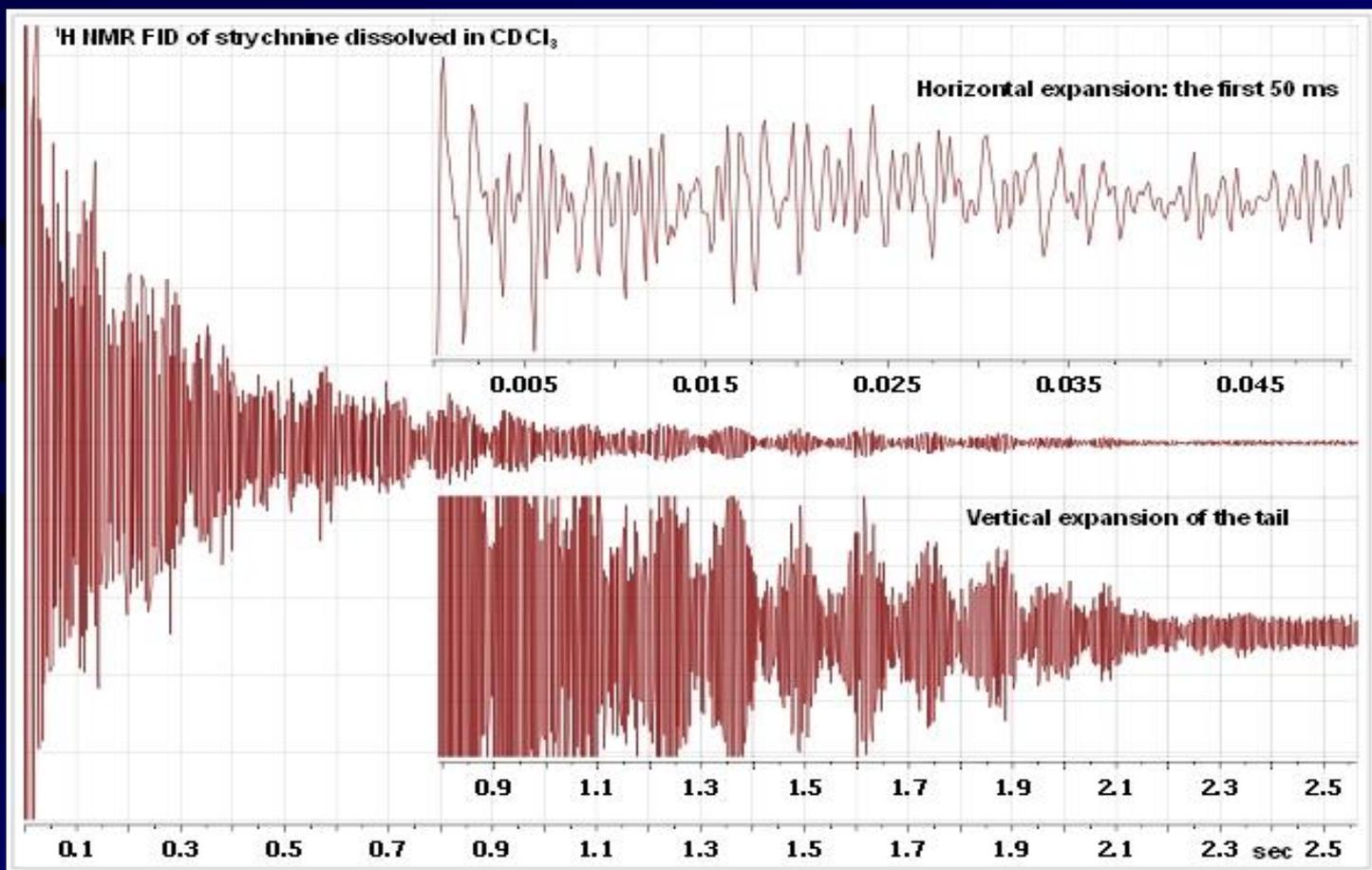
Ortho-di-chloro-benzene (ODCB)

Resolution: about 0.10 Hz

Courtesy: Prof. Lodovico Lunazzi, University of Bologna

The pulsed FT era: ~ 1968 ... to today

A strong (over 100 W) **RF pulse** is applied to the coil for a brief period (in this case 10 μ s). Thereafter, a weak transient signal called **free induction decay (FID)** corresponding to the transversal magnetization component is detected. Depending upon the sample and upon field homogeneity, this can last from a few microseconds (solids) up to many minutes (liquids). In this strychnine solution it took 2.5 seconds.

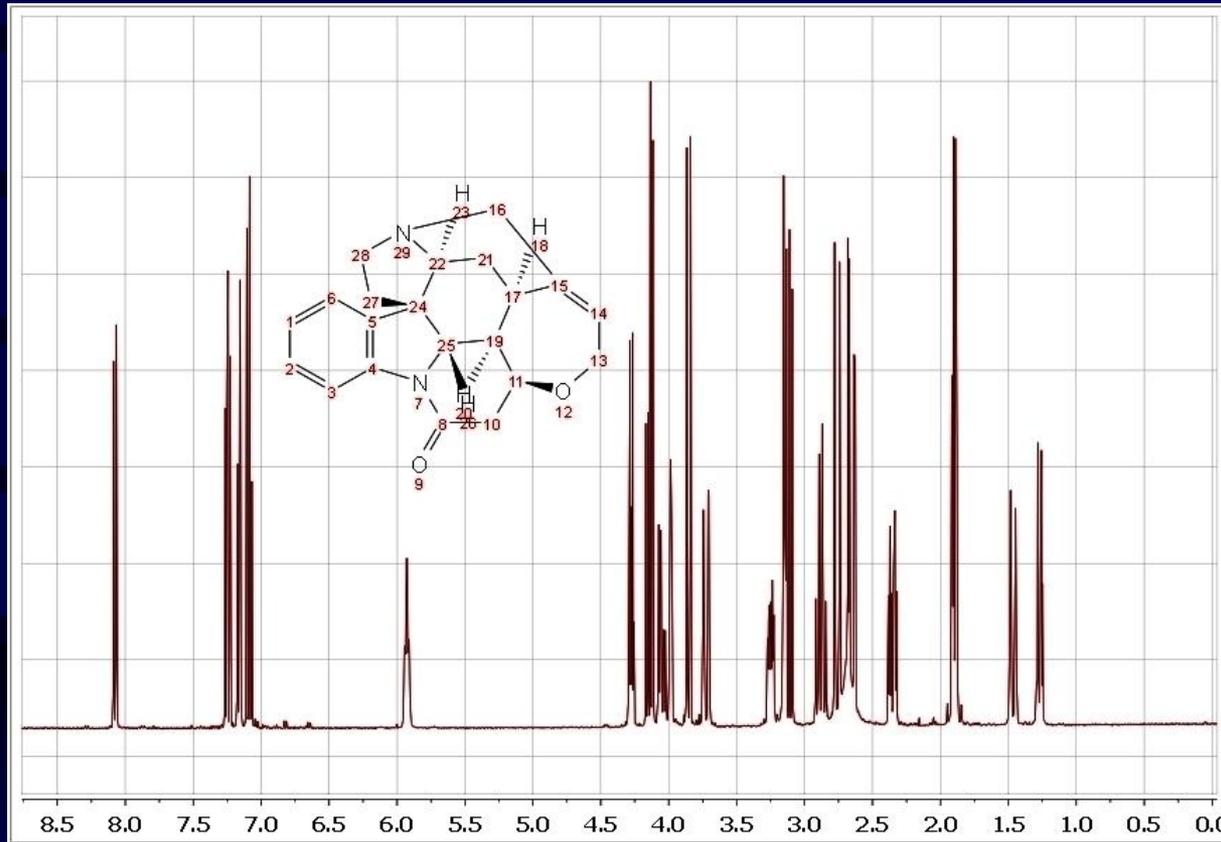


... **50 years** (and thousands of Theses) **after the discovery**



A NMR data example: the spectrum

Applying the Fourier Transform to the FID data, one separates the individual component signals with different Larmor frequencies and thus obtains the spectrum.



Anticipation: why are there different spectral components? Because each proton in the molecule is subject to a different **screening** by the binding electrons. But be careful: the scale is in **ppm** of the carrier frequency! A tiniest of effects!

**Can we understand, and simulate,
the intricate high-resolution NMR spectra?**

YES ! (well, almost)

Thanks to

Weston Anderson, John Roberts,

and a handful of others who introduced the
most unusual concept of Spin Hamiltonian
and discovered its terms and their math forms

2011: Stan meets Weston!

1964, Prague: I learn how to simulate NMR spectra (on Zuse-25 and then on Minsk-22 computers), studying Weston's papers.

I return to it many times:

1975, with Peter Diehl, in Basel

2006, with the Mestrelab Research guys

... and it ain't finished yet

Thanks, my Teacher!



Discussion ☺

B. Uphill to Spin Hamiltonian

Don't ask me what is Hamiltonian, else I will cry!

Basically, it is the grand total of all energy terms in a physical system.

In both classical and quantum physics, it also defines the evolution of the system when left alone.

Know thy Hamiltonian and you will die a happy person!

What is so special about Spin?

Spin is a **degree of freedom**, but it is not like any other classical «coordinate». Indeed, we know nothing about the «space» it spans. All we know is that:

- It is **genuinely quantum**. A single particle, whenever measured, is always found in one of a **finite number of eigenstates** ($2S+1$, where the half-integer constant S is said to be the particle's spin). Consequently, the Hilbert space spanned by linear combinations (with complex coefficients) of the eigenstates is **finite-dimensional**. All this is impossible in classical systems.
- It is associated with **persistent intrinsic angular momentum** vector, something unknown in classical physics. While the magnitude of the vector is constant, its orientation (for example, a projection on a reference axis) can assume exactly $2S+1$ distinct values.
- It transforms under rotations as an **axial vector**. Under rotations and compositions, a particle with spin S behaves as belonging to the irreducible SO_3 representation with trace S . Unlike anything classical, **this covers also the half-integer SO_3 representations**.
- A particle with a non-zero spin S always exhibits a **magnetic moment** (again an axial vector), which is **strictly aligned** with the angular momentum, but whose value, while characteristic of each particle kind, seem to be totally independent of S .

Spin-space versus classical-space

Let s be a «spin coordinate» of a particle with spin S , and let q be one of its space coordinate. We see that:

- s is inaccessible and hypothetical
- Expressions involving ∂s or ds have no sense. E.g., there is no s -velocity $\partial s/\partial t$
- A function $f(s)$ is void of sense
- No Hamiltonian H can not be defined in terms of s and a generalized s -momentum
- One defines a Hilbert space spanned by linear combinations of a finite set of base functions $|n\rangle$ of which no detail is known
- Quantum Hamiltonian \mathbf{H} is defined directly by its action on $|n\rangle$
- Only quantum treatment is possible, in which only the actions of \mathbf{H} on the elements of the Hilbert space matter.

- q is accessible to measurements
- Expressions involving ∂q or dq are common. E.g., $\partial q/\partial t$ is the velocity
- A function $f(q)$ is a common concept
- A Hamiltonian H is defined in terms of generalized q -velocity and q -momentum
- One derives a Hilbert space of suitable functions spanned by linear combinations of an infinite set of base functions $\psi_n(\mathbf{x})$
- There is a recipe to convert a Hamiltonian into a quantum Hamiltonian operator \mathbf{H}
- In quantum treatment, from now on, only the actions of \mathbf{H} on the elements of the Hilbert space matter.

Different starting paths but, finally, the same quantum apparatus !

**In short:
there is no classical Spin Physics!**

The amazing Q*S factorization: the emergence of Spin Hamiltonian

- In general, spins interact extremely weakly with all other degrees of freedom (the so-called «lattice»). This is best testified by the low (RF) frequencies of interacting electromagnetic fields, as well as the very long relaxation times.
- The long relaxation times also mean that all interactions with the «lattice» are time-averaged, except for the slowest motions.
- All this indicates the possibility to «factorize» a system's quantum space into two separate spaces with apparently independent evolutions: the «normal» one with states based on coordinates & momenta, and the one based on spin-states.

Schematically: $\Psi(q,s) \cong \psi(q) \sigma(s)$ and $\mathbf{H} \Psi(q,s) \cong \{\mathbf{H}_Q \psi(q,S)\} \{\mathbf{H}_S \sigma(s,Q)\}$

This resembles the arguments behind Born-Oppenheimer approximation in molecular physics.

The spin Hamiltonian \mathbf{H}_S contains only spin operators, combined with plain numeric parameters whose values depend upon the Q-state of the system (for several reasons, such as entropic effects due to the exclusion principle, this is not so simple for \mathbf{H}_Q).

Spin Hamiltonian: a pleasant surprize

Here enters the disarming geniality of Weston Anderson.

Being practical, he tried and discarded completely the classical part.

And it worked! In a spin space which nobody could even imagine!

But it soon allowed to explain the spectra of chemical compounds.

It was first opposed and criticised;

but it worked so well that the critical voices soon died out.

Especially since it was *the only* thing that worked.

All chemical applications of NMR depend on it!

Elementary spin operators: where do they come from?

Consider a particle with an N -dimensional space of spin states ($N = 2S+1$).

It can be shown that any physical system whose associated quantum-mechanical Hilbert space H is finite-dimensional admits a complete set of operators on H which match the commutation relations of the infinitesimal generators of $SO(3)$ rotations group.

In other words, pure mathematics shows that every finite-dimensional Hilbert space can be interpreted as a spin space! Ref: *Sykora*, DOI [10.3247/SL1Phys06.001](https://doi.org/10.3247/SL1Phys06.001)

These operators on H , hence called spin operators, are unique for any choice of base states in H , up to an arbitrary common phase factor (chosen to be 1.0)

A convenient choice of the base states matches those observed for an **isolated spin particle in a strong magnetic field** with elements, hence called spin states, labeled as $|m\rangle$, where $m = -S, -S+1, \dots, S-1, S$

The unique “elementary” spin operators (apart from identity) are then always three, regardless of the spin S , and denoted as $\{S_x, S_y, S_z\}$ or, equivalently, as $\{S^+, S^-, S_z\}$

The definitions and properties of these spin operators are listed on the next slide.

Elementary spin operators: properties

Auxiliaries:

$$S^+ \equiv S_x + iS_y, \quad S^- \equiv S_x - iS_y, \quad S_x \equiv (S^+ + S^-)/2, \quad S_y \equiv (S^+ - S^-)/2i$$

Functional definitions:

$$S_z|m) = m|m), \quad S^\pm|m) = \sqrt{(S \mp m)(S \pm m + 1)} |m \pm 1)$$

Properties:

$$S \cdot S = S_x S_x + S_y S_y + S_z S_z = (S^+ S^- + S^- S^+)/2 + S_z S_z = S(S + 1) = \text{const}$$

Commutators:

$$[S_x, S_y] = iS_z, \quad [S_y, S_z] = iS_x, \quad [S_z, S_x] = iS_y$$

$$[S_z, S^\pm] = \pm S^\pm, \quad [S^+, S^-] = 2S_z$$

Spin Hamiltonian: many interaction terms

Note: indices refer to nuclei and/electrons and imply summations

$$H = H_Z + H_{SR} + H_C + H_{DD} + H_{DE} + H_F + H_J + H_Q$$

- $H_Z = -\hbar\gamma_i \mathbf{B} \cdot \mathbf{I}_i$, **Zeeman term**
 \mathbf{B} is the **magnetic field** at the nucleus location, $\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1 + \mathbf{B}_2 + \dots + \mathbf{G}_0 + \mathbf{G}$
- $H_{SR} = \mathbf{M} \cdot \mathbf{R}_i \cdot \mathbf{I}_i$, **Spin-rotation term**
 \mathbf{M} is the **molecular angular momentum** and \mathbf{R}_i is a spin-rotation tensor.
- $H_C = \mathbf{B} \cdot \mathbf{C}_i \cdot \mathbf{I}_i$, **Chemical shifts (screening) term**
 \mathbf{C}_i is the **chemical shift tensor** due to the *molecular polarization* in the field \mathbf{B} .
- $H_{DD} = \mathbf{I}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{I}_j$, **Direct dipole-dipole interactions term**
 \mathbf{D}_{ij} is the **dipole-dipole interaction tensor** of the *direct* dipolar coupling between the magnetic moments of the nuclei i, j .
- $H_{DE} = \mathbf{I}_i \cdot \mathbf{E}_{ij} \cdot \mathbf{S}_v$, **Dtto between nuclei and free electrons**
 \mathbf{E}_{ij} is the tensor of the **direct dipolar interaction** between the nucleus i and the spin \mathbf{S}_v of an *unpaired electron* v .
- $H_F = \mathbf{I}_i \cdot \mathbf{A}_{iv} \cdot \mathbf{S}_v$, **Hyperfine couplings term (with free electrons)**
 \mathbf{A}_{iv} is the **hyperfine coupling tensor** due to the *contact (Fermi) interaction* between the nucleus i and an *unpaired electron* v .
- $H_J = \mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j$, **Indirect couplings term**
 \mathbf{J}_{ij} is the **indirect coupling tensor** arising from the *Fermi contact* between the nuclei i, j and the shared *chemical bond electrons*.
- $H_Q = \mathbf{I}_i \cdot \mathbf{Q}_i \cdot \mathbf{I}_i$, **Quadrupole interactions term**
 \mathbf{Q}_i is the tensor describing the coupling between a *local molecular electric field gradient* and the *electric quadrupole moment* of the nucleus i .

Spin Hamiltonian: many known interaction terms

$$H = H_Z + H_{SR} + H_C + H_{DD} + H_{DE} + H_F + H_J + H_Q$$

Behind each term, there are the names of those who elucidated it

Each elementary term is an inner product of one or two spin operators with a tensor of rank 1 or 2, intended as a mere numeric parameter

Hence the term «spin-system parameters», such as shifts as J's
To compute those, one must use the Q-space quantum mechanics,
a demanding task sometimes called «predictions».
More often they are determined empirically.

Spin Hamiltonian: dirty tricks to define the terms

How were most of the spin hamiltonian terms constructed?

Example #1: Zeeman interaction of a spin particle with a magnetic field

Classical interaction between a magnetic moment $\boldsymbol{\mu}$ and a magnetic field \mathbf{B} :

$$E = -\mathbf{B} \cdot \boldsymbol{\mu}$$

Replace the magnetic moment $\boldsymbol{\mu}$ with $\gamma\mathbf{M}$, γ being the gyromagnetic ratio, and \mathbf{M} the intrinsic angular momentum of the particle:

$$E = -\gamma \mathbf{B} \cdot \mathbf{M}$$

Replace the angular momentum with its quantized version $\mathbf{M} = \hbar\mathbf{S}$, et voilà:

$$E = -\gamma\hbar \mathbf{B} \cdot \mathbf{S}$$

Wait! Is this fair ???

The first equation is classical, not quantized, the last one is quantized!

Rigorously speaking, it is not fair! It is a dirty trick! But it works!

Spin Hamiltonian: more dirty tricks

Example #2: Dipole-dipole interaction between two spin particles (1 and 2)

Classical interaction between two magnetic dipole moments μ_1 and μ_2 separated by a space-vector \mathbf{r} :

$$E = - (1/4\pi) \mu_1 \cdot [(3\mathbf{r}\mathbf{r} - r^2) / r^5] \cdot \mu_2$$

Replace every μ with corresponding $\gamma\hbar\mathbf{S}$:

$$E = - (\hbar\gamma_1\gamma_2/4\pi) \mathbf{S}_1 \cdot [(3\mathbf{r}\mathbf{r} - r^2) / r^5] \cdot \mathbf{S}_2 = \mathbf{S}_1 \cdot \mathbf{D}_{12} \cdot \mathbf{S}_2$$

Where the dipole-dipole interaction tensor \mathbf{D}_{12} is

$$\mathbf{D}_{12} = - (\hbar\gamma_1\gamma_2/4\pi) [3\mathbf{r}\mathbf{r} - r^2] / r^5$$

And from now on, we keep handling \mathbf{D}_{12} in a classical way (for example, applying all kinds of averaging) and the spin operators in a quantum way!

Elementary, very intuitive, and very useful? Yes!

But very questionable, too!

Spin Hamiltonian: the «liquid state NMR spectroscopy» variety

Most molecules of interest to an organic chemist are

- diamagnetic (no free electrons),
- have only nuclei with spin $1/2$ (no quadrupole moments),
- and are measured in solution where they tumble in a fast and random way which averages to zero all traceless parts of second rank tensors, leaving only the rotation-invariant scalar part (one third of their trace).

How does the Spin Hamiltonian reduce under these conditions?

Spin Hamiltonian: the organic chemist's fast-food variety

$$\mathbf{H} = \mathbf{H}_Z + \mathbf{H}_{SR} + \mathbf{H}_C + \mathbf{H}_{DD} + \mathbf{H}_{DE} + \mathbf{H}_F + \mathbf{H}_J + \mathbf{H}_Q$$

- $\mathbf{H}_Z = -\hbar\gamma_i \mathbf{B} \cdot \mathbf{I}_i$, Zeeman term
Considered as a constant offset. De-facto removed by spectral referencing.
- $\mathbf{H}_{SR} = \mathbf{M} \cdot \mathbf{R}_i \cdot \mathbf{I}_i$, Spin-rotation term
Averages to zero under fast tumbling
- $\mathbf{H}_C = \mathbf{B} \cdot \mathbf{C}_i \cdot \mathbf{I}_i$, **Chemical shifts (screening) term**
All tensors reduce to scalars (chemical shifts)
- $\mathbf{H}_{DD} = \mathbf{I}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{I}_j$, Direct dipole-dipole interactions term
Averages to zero under fast tumbling
- $\mathbf{H}_{DE} = \mathbf{I}_i \cdot \mathbf{E}_{ij} \cdot \mathbf{S}_v$, Dtto between nuclei and free electrons
Absent (no free electrons)
- $\mathbf{H}_F = \mathbf{I}_i \cdot \mathbf{A}_{iv} \cdot \mathbf{S}_v$, Hyperfine couplings term (with free electrons)
Absent (no free electrons)
- $\mathbf{H}_J = \mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j$, **Indirect couplings term**
All tensors reduce to scalars (J couplings)
- $\mathbf{H}_Q = \mathbf{I}_i \cdot \mathbf{Q}_i \cdot \mathbf{I}_i$, Quadrupole interactions term
Averages to zero under fast tumbling

Spin Hamiltonian: the organic chemist's variety in explicit form

$$H = \sum_{i=1}^n (\delta_i B_0) S_z + \sum_{i=1}^n \sum_{j=i+1}^n J_{ij} S_i \cdot S_j$$

For n nuclei, this spin Hamiltonian contains:

At most n chemical shifts and at most $n(n-1)/2$ coupling constants J

Typical values:

for 3 nuclei: max 3 shifts, 3 J 's; for 20 nuclei: max 20 shifts, 190 J 's

In practice, the number of distinct shifts is reduced by molecular symmetry, and the number of non-zero J 's is very much reduced by structural distance.

The pattern of missing J 's defines the spin system types.

Spin Hamiltonian:

thanks God we had low fields first and high fields later!

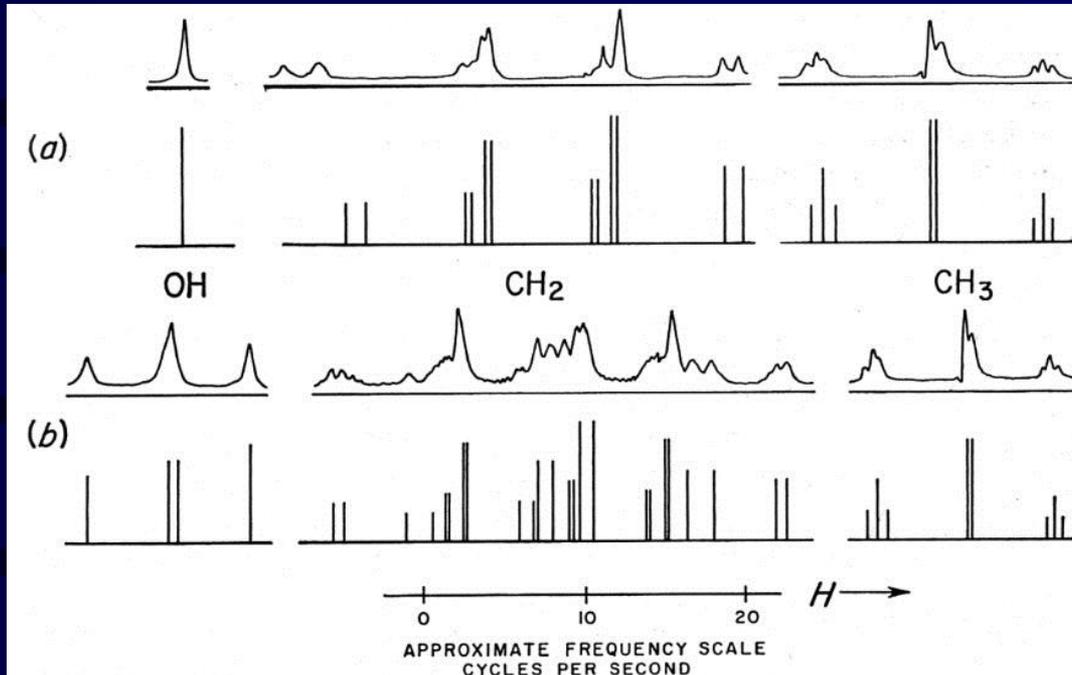


FIG. 6-19. High-resolution spectrum of the hydroxyl, methylene, and methyl protons of ethyl alcohol in sequence from left to right (a) for acidified alcohol and (b) for pure alcohol. Theoretical spectra calculated by second-order perturbation theory are given below. (Arnold.²⁰)

30 MHz spectrum, but with a linewidth below 0.2 Hz

To elucidate the form of small terms like J-couplings,
low but very homogeneous field were better !!!

Discussion ☺

C. Downhill to Spectra

Now that we know the Spin Hamiltonian,
and even have the formulas for its matrix elements,
computing its spectrum is a routine job.

Homework!

Spin Hamiltonian: base spin states

We already saw the base states on a single spin:

$$|m\rangle, \quad m = -S, -S+1, \dots, S-1, S.$$

For $S = 1/2$ we can write $|0\rangle$ for $m = -1/2$ and $|1\rangle$ for $m = +1/2$

These spin states form, by definition, a complete, orthonormal set.

For a spin system with n nuclei, a complete orthonormal set can be build by taking all possible products of the single-spin base functions:

$$|m_1\rangle |m_2\rangle \dots |m_n\rangle, \text{ running over all possible combinations of all the } m_i$$

For $S = 1/2$ these can be encoded as n -digit binary integers $|01\dots 0\rangle$

In general, there are 2^n base functions for a system of n spin $1/2$ nuclei. This defines also the total dimension of the corresponding spin Hamiltonian matrix.

Examples:

for an AB system of 2 nuclei, we have 4 base functions, namely

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

for an ABC system of 3 nuclei, we have 8 base functions, namely

$$|000\rangle, |001\rangle, |010\rangle, |100\rangle, |011\rangle, |101\rangle, |110\rangle, |111\rangle$$

Spin Hamiltonian: the matrix form

We already saw the action of elementary spin operators on the single-spin base states. From that it is easy to work out a simple recipe for building the spin Hamiltonian matrix for a system of n spin $1/2$ nuclei in a liquid-state sample:

Consider the element

$$H_{K,L} \equiv \langle K | \mathbf{H} | L \rangle, \text{ where } |K\rangle \text{ and } |L\rangle \text{ are encoded as } n\text{-digit binary numbers}$$

The following rules apply:

1. When $K \neq L$ (off-diagonal terms), $H_{K,L} = 0$ if $|K\rangle$ and $|L\rangle$ have a different number of binary digits set to 1 (the same total S_z). This efficiently factorizes the H-matrix according to total S_z – a universal property due to the fact that total S_z commutes with the spin Hamiltonian. This, however, is included in a still more stringent rule: $H_{K,L} = 0$ if $|K\rangle$ and $|L\rangle$ differ in more, or less, than two «digits». If they differ in the pair of digits i and j , then $H_{K,L} = J_{ij}/2$.
2. When $K = L$ (diagonal terms), $H_{K,L}$ is the sum of (a) all chemical shifts, each taken with a factor $-1/2$ if the corresponding digit in $|K\rangle$ is 0 and $+1/2$ if it is 1, and (b) all J_{ij} multiplied by $-1/4$ if the digits corresponding to nuclei i,j in $|K\rangle$ match or $+1/4$ if they do not match.

ABC-system spin Hamiltonian matrix: the S_z manifolds and examples of matrix elements

K\L	111	110	101	011	100	010	001	000
111								
110								
101								
011								
100								
010								
001								
000								



$$(101|H|101) = (s_A - s_B + s_C)/2 + (-J_{AB} + J_{AC} - J_{BC})/4$$



$$(101|H|011) = J_{AB}/2$$

Spin Hamiltonian: eigenstates, eigenvalues, and eigenvectors

These are obtained by diagonalizing the spin Hamiltonian matrix
(exploiting also the S_z factorization)

There are as many eigenstates as the full dimension of the matrix
(for example 1024 for a 10-spin system)

Each eigenstate defines an energy level (the eigenvalue) and is associated with an mixed spin state, which is a linear combination of the base spin states (with coefficients defined by the eigenvectors)

Spin Hamiltonian: spectral transitions

Consider two eigenstates with energy levels E_a and E_b (expressed in frequency units) and eigenvectors U_a and U_b .

These define potentially a spectral transition such that:

- The transition frequency is: $E_a - E_b$
- The transition intensity is: $|(U_a | S^+ | U_a)|^2$

Rules just as simple as those for the matrix elements can be worked out also for transition intensities.

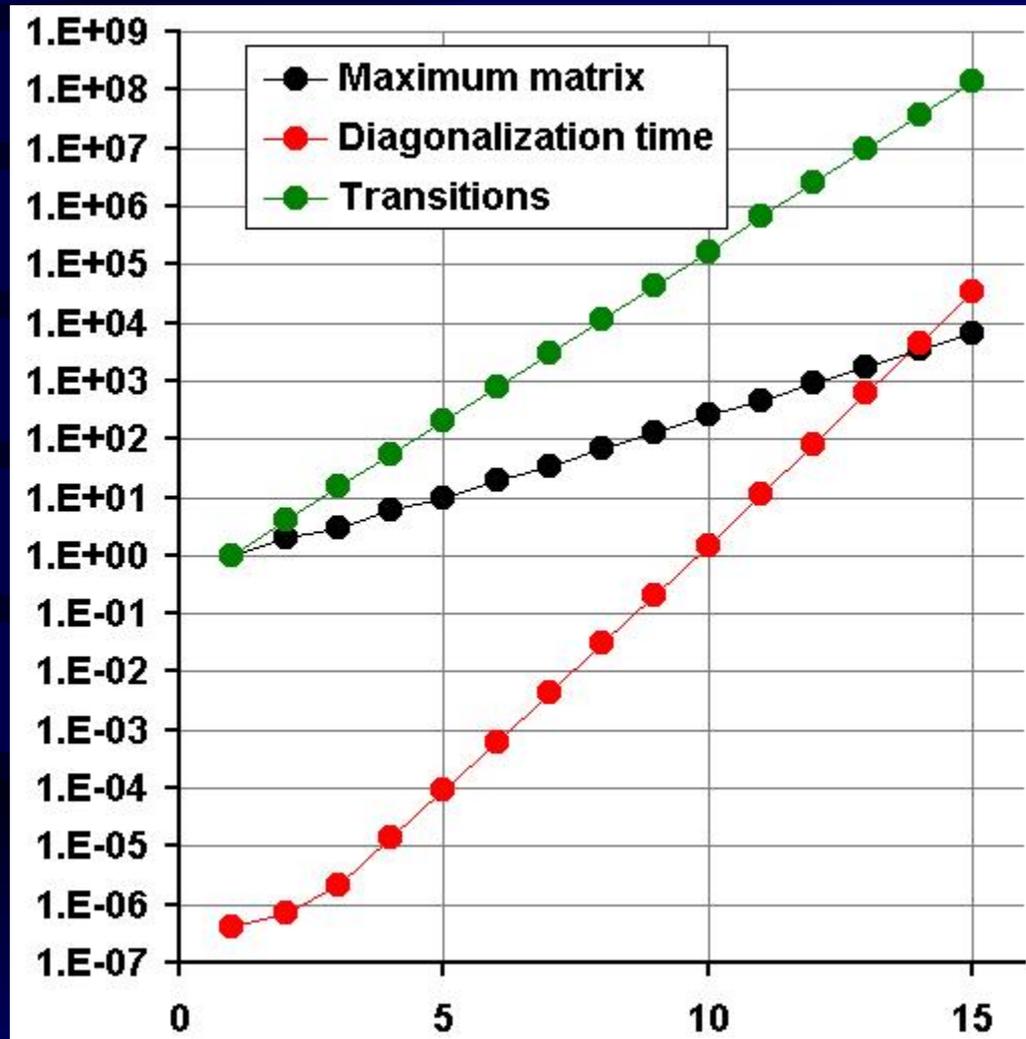
Spectrum: finally!

A spectrum is simply a superposition of all spectral transitions

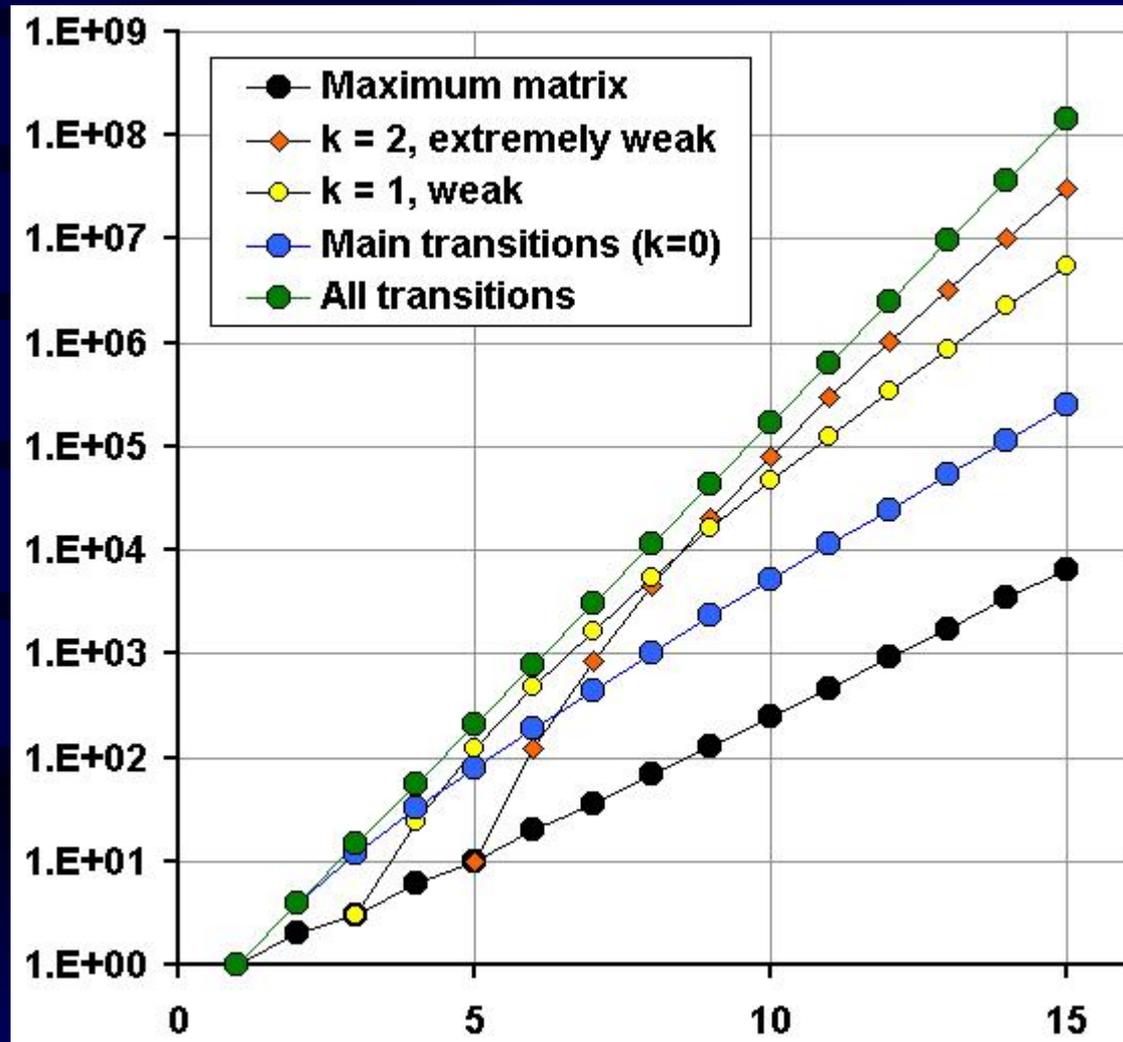
Cool, isn't it!

Transitions compose peaks,
peaks group into multiplets, and
multiplets compose the spectrum

Simulating spectra: doing it in earnest



Simulating spectra: counting transitions



Simulating spectra: conclusions

Despite all the approximations, simulating real spectra in this way is still not simple and requitres additional tools and tricks.

Next time!

Discussion ☺

What was left out ?

- Treats and tricks (I tried to fit it in, but no way ... website)
- Axially oriented systems (molecules in liquid crystals)
- Spectral moments and multiplets moments
- Simulations of 2D, 3D, ... spectra
- Fitting of spectral parameters
- Dynamic systems (chemical exchange)
- Liouville space treatment
- Other simulation approaches
- Decoupling, spin tickling, polarization transfer
- Solid-state NMR (MAS and CP-MAS)
- NMR of solids
- Etc

Thank You for your Attention

These slides are now online:

DOI [10.3247/SL4Nmr13.005](https://doi.org/10.3247/SL4Nmr13.005)