

# Tutorial on Spin Systems in Magnetic Resonance

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I am a physicist, an NMR buff, a programmer and a retired but busy Italian entrepreneur.

But I started in Prague and it is nice to return back occasionally!



*21 August 1968: the Soviet invasion*

# Tutorial on Spin Systems in 40 minutes?

Come on!

The Organizers got something wrong!

All I can promise is that I will try my best

The goal is to catch your fancy and to show you that

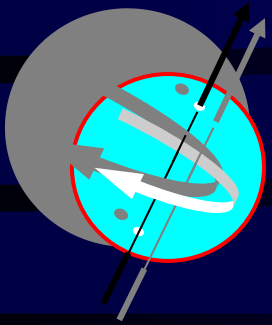
**Spins are a great Fun, much better than Sex**

The four Sections I would have liked to go through:

- Generalities
- From Spin Hamiltonian to Spectra
- ~~Molecular NMR Spectra in Isotropic Solutions~~
- ~~Special Effects and Systems~~

*Note: the barred items will be for some other time*

# I. GENERALITIES



# What the Hell is Spin?

Spin  $S$  [dimensionless, half-integer]

Angular momentum ...  $m = \hbar S$  [ J s ]

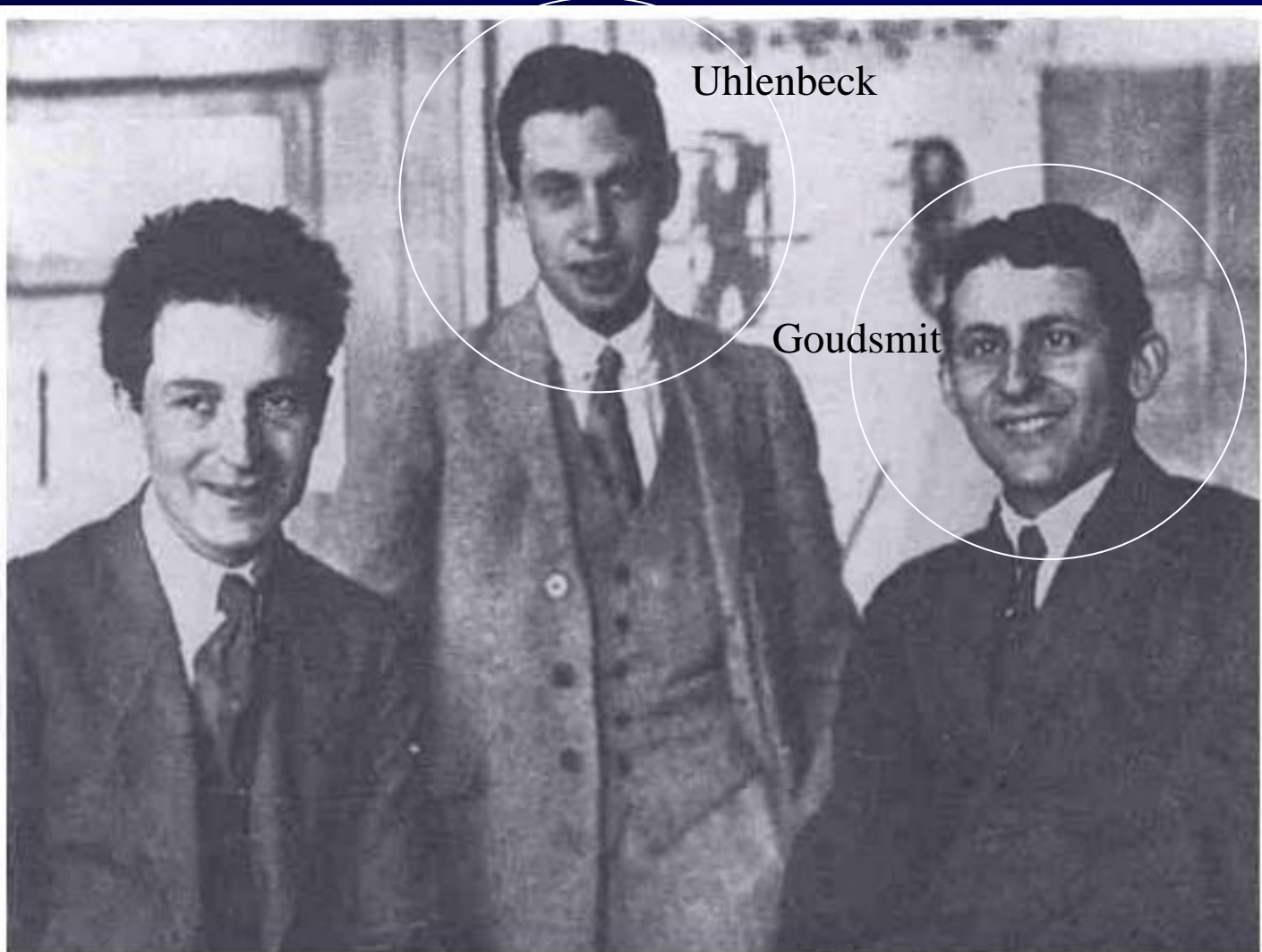
- It has to do with the **mechanical angular momentum** of (small) bodies, which turns out to come only in multiples of the **Planck constant** (nobody knows why)
- By definition, the half integer multiple is called the “spin”  $S$  of a body.
- The spin is an **intrinsic** and **persistent** property. Bodies with  $S > 0$  just can't stop spinning. Any proton, for example, spins at the same rate since the Big Bang (nobody knows why)! If it stopped spinning, it would stop being proton.
- Half-integer spins can not be due to something orbiting inside the body, since *orbital angular momenta can have only integer spin values*.

**And so on: from Mystery to shining Mystery!**

# 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 pioneers (electron spin)



1926: Oscar Klein, George E. Uhlenbeck, and Samuel A. Goudsmit.  
Courtesy of [AIP Emilio Segré Visual Archives](#)

# What other properties do particles have?

Magnetic dipole moment  $\mu = \gamma \mathbf{m}$  [A m<sup>2</sup>] or [J T<sup>-1</sup>]

Particle 	Spin	$\gamma$ [MHz/T]
<sup>0</sup> e Electron	1/2	-28024.953
<sup>0</sup> $\mu$ Muon	1/2	-135.539
<sup>3</sup> H Triton	1/2	+45.415
<sup>1</sup> H Proton	1/2	+42.577
<sup>3</sup> He Helion	1/2	-32.434
<sup>1</sup> n Neutron	1/2	-29.165
<sup>2</sup> D Deuteron	1	+6.536

... and all other magnetic nuclides ...

**More mysteries:** theoretical physics can reproduce the electron magnetic moment with amazing precision (12 digits), that of the muon so-so, that of the proton with >100% error, and those of nuclides, well, forget it!

# The dawn of nuclear spins & magnetic moments

- 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 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 the neutron (L.W. Alvarez, F. Bloch, 1940)

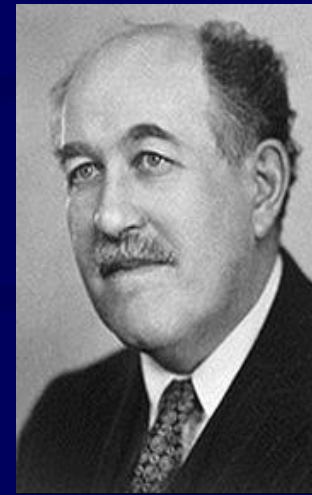


# More pioneers (nuclear spin)

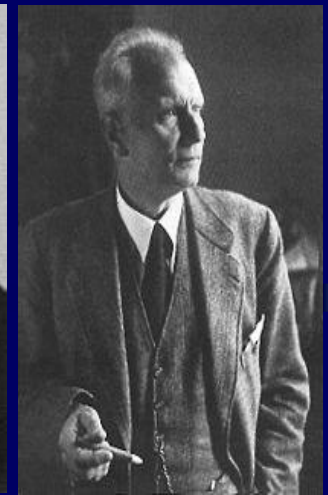
Dennison,  $^1\text{H}$  spin      Kronig, e-spin, really



1925      From left: Yoshio Nishina (1890–1951), David M. Dennison (1900–1976), Werner Kuhn (1899–1963), Ralph de Laer Kronig (1904–1995), Bidu Bhusan (B.B.) Ray in Copenhagen.



Otto Stern



Walter Gerlach



Isidor Isaac Rabi  
Magnetic Resonance

# Which particles are observable in Magnetic Resonance?

## Properties of nuclides



Chemical element symbol	X
Number of protons (atomic number)	Z (defines the element)
Electric charge (e = charge of electron)	$Q = -Ze$ [C]
Number of neutrons	N
Mass number (number of nucleons)	$A=N+Z$
Symbol of the nuclide	${}^A X$
Natural abundance	a [%]
Mass	M [kg]
Global binding energy	$E = (Zm_p + Nm_n - M)c^2$ [J]
<b>Spin (the magnitude of vector S)</b>	<b><math>S = 0, 1/2, 1, 3/2, 2, \dots</math></b>
Angular momentum	$m = \hbar S$ [J s]
Electric dipole	always null
<b>Magnetic dipole</b>	<b><math>\mu = \gamma m</math> [A m<sup>2</sup>] or [J T<sup>-1</sup>]</b>
<b>Gyromagnetic ratio</b>	<b><math>\gamma</math> [rad s<sup>-1</sup> T<sup>-1</sup>] or [Hz T<sup>-1</sup>]</b>
g-factor ( $\mu_N =$ Bohr's nuclear magneton)	$g =  \mu  / S\mu_N = \hbar\gamma / \mu_N$
Electric quadrupole moment	q [Cm <sup>2</sup> ] ( $\neq 0$ iff $S \geq 1$ )
For unstable nuclides:	
Half-life period	$T_{1/2}$ [s]
Decay mode(s)	$\alpha, \beta, \gamma, \beta$ -capture, ...
Nuclear structure	
Energy of the 1st excited state	$E^* - E_0$ [J]
etc., etc., etc.	

Only particles and nuclides with nonzero spin S have a magnetic moment and therefore are observable in Magnetic Resonance.

Counting the stable, and the reasonably stable, nuclides, the total is 83.

Of these, the most interesting are those that:

- Have spin  $1/2$  ( $\Rightarrow$  no quadrupole moment)
- Have a large gyromagnetic ratio  $\gamma$
- Are isotopically abundant
- Are present at important concentrations in living tissues and/or in pharma products

This leaves mostly:  ${}^1\text{H}$ ,  ${}^{19}\text{F}$ ,  ${}^{31}\text{P}$ , ...

But these also get some attention:  ${}^{13}\text{C}$ ,  ${}^{23}\text{Na}$ , ...

Plus, there are always special applications involving many other nuclides.

# Can we exploit it, despite our ignorance? Sure, as always:

## APPLICATIONS ...

<b>NMR</b>	Nuclear Magnetic Resonance
<b>EMR</b>	Electron Magnetic Resonance (EPR / ESR)
<b><math>\mu</math>MR</b>	Muon Magnetic Resonance
<b>NQR</b>	Nuclear Quadrupole Resonance
<b>FMR</b>	Ferro (anti-ferro) Magnetic Resonance
<b>MRI</b>	Magnetic Resonance Imaging
<b>MRFM</b>	Magnetic Resonance Force Microscopy
etc. ...	including double- and triple-combinations

## ... and their BRANCHES:

nuclide(s):	$^1\text{H}$ , $^{13}\text{C}$ , $^2\text{D}$ , $^{31}\text{P}$ , $^{23}\text{Na}$ , $^{15}\text{N}$ , $^{14}\text{N}$ , $^{19}\text{F}$ , $^{29}\text{Si}$ , ... + combinations
excitation:	CW, Pulsed, Hadamard, Noise excited, DNP, ...
detection:	Induction, Direct/Indirect, Optical, Force, ...
field type:	High/Low value, High/Low resolution, Ex-situ, ...
signal type:	Time/Frequency domain
methodology:	Spectroscopy (1D, 2D, ..., DOSY, ...) Relaxometry (at fixed or variable field) ... Logging (such as well-logging), ...
object:	Chemical compounds, Proteins, Tissues, Materials, ...
context:	In-vitro / In-vivo, Large scale (geophysical)

# How do nuclides interact with the outside World?

There is only one way:

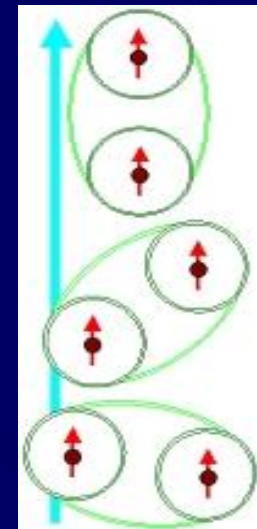
A nuclide interacts with the electromagnetic field present at the place where the it is located.

It has absolutely NO IDEA of WHERE THE EMF FIELD CAME FROM, whether

- from the atomic or molecular electron envelope
- a neighboring magnetic nuclide,
- an internal field of a crystal,
- or an externally imposed field such as that of a magnet (maybe the Earth)

This is important to understand, because otherwise it is impossible to grasp most of MR

Example: when, in a magnet, a molecule rotates, the spin vectors of its nuclei stay locked to the dominant external field; they **DO NOT** rotate with the molecule. If that is not clear, you would never understand why dipolar interactions out in liquids, nor why MAS works!



# How do nuclides interact with the outside World?

For spin  $S = 1/2$  nuclei, the only possible interaction is with the magnetic field.

For nuclides with spin  $S \geq 1$  and an appreciable quadrupole moment, there is also the interaction with local electric field gradients. Such gradients are in general due the local molecular electric fields and in some cases can become dominant. In such cases the nuclear spins DO rotate with the molecule.

Consequently, NMR of nuclides with spin  $S \geq 1$  is much more complicated than for  $S = 1/2$  (there is a smooth transition between NMR and NQR).

Non-magnetic nuclides with spin  $S = 0$  (such as  $^{12}\text{C}$ ) do not interact at all and are totally invisible to NMR.

## Do nuclides interact with each other?

The magnetic ones with  $S > 0$  yes, but only indirectly

There exist two different mechanisms:

**First** we have the direct dipolar interaction due to the magnetic field produced by the magnetic dipole of one nuclide and perceived by another one. Since a dipolar field drops with the cube of the distance, such interactions are short-ranged (less than 1 nm). Moreover, the interaction depends also on the *direction* of the vector between the locations of the two nuclei; it is in fact described by a traceless tensor which under fast random molecular reorientation averages to zero.

**Second** mechanism is quantum and has to do with the probability that an electron (also a magnetic particle) is simultaneously present at the location of both nuclei (the so-called **Fermi term**). This provides a mediated coupling between the two close-enough nuclei which turns out to be also a tensor, but not a traceless one. Its average value over all molecular orientations is a non-zero scalar known as the “indirect coupling” or “scalar coupling” or simply “J-coupling”.

# Spin is Quantized!

The founding fathers of NMR knew this well from theory and they the **basic properties of quantum operators describing a particle with spin S:**

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:

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

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:

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

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

# The dirty ways of Quantization

Ok, a single spin is quantized, but how does one quantize all the other terms needed to describe spin-system interactions?

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

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

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

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

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

c. 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 a dirty trick! But it works!



# More dirty ways of Quantization

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

a. Classical interaction between two magnetic dipole moments  $\mu_1$  and  $\mu_2$  separated by a space-vector  $\mathbf{r}$  :

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

b. Replace every  $\mu$  with a 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

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

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 rather questionable, too!

## The heretic Spin Hamiltonian and its Father

In 1950's Weston Anderson, an experimentalist and a partner of Varian Associates, in an effort to figure out the spectra of chemical compounds, developed the weird concept of a spin Hamiltonian acting only on the spin degrees of freedom of a system, completely factorized from all other degrees of freedom (particle locations and velocities).

The concept was viewed as a heresy. Serious physicists would always start from a full description (and usually get lost in it!)

But Weston's approach worked (and it is still working)!

**For me, Weston is the Father of Spin Hamiltonian =====>**



2009

# Spin Hamiltonian with (almost) all the known terms

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

$$H_Z = -\hbar\gamma_i \mathbf{B} \cdot \mathbf{I}_i, \quad \text{Zeeman term}$$

$\mathbf{B}$  is the **magnetic field** at the nucleus location,  $\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1 + \mathbf{B}_2 + \dots + \mathbf{G}_0 + \mathbf{G}$

$$H_{SR} = \mathbf{M} \cdot \mathbf{R}_i \cdot \mathbf{I}_i, \quad \text{Spin-rotation term}$$

$\mathbf{M}$  is the **molecular angular momentum** and  $\mathbf{R}_i$  is a spin-rotation tensor.

$$H_C = \mathbf{B} \cdot \mathbf{C}_i \cdot \mathbf{I}_i, \quad \text{Chemical shifts (screening) term}$$

$C_i$  is the **chemical shift tensor** due to the *molecular polarization* in the field  $\mathbf{B}$ .

$$H_{DD} = \mathbf{I}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{I}_j, \quad \text{Direct dipole-dipole interactions term}$$

$D_{ij}$  is the **dipole-dipole interaction tensor** of the *direct* dipolar coupling between the magnetic moments of the nuclei  $i, j$ .

$$H_{DE} = \mathbf{I}_i \cdot \mathbf{E}_{ij} \cdot \mathbf{S}_v, \quad \text{Ditto between nuclei and free electrons}$$

$E_{ij}$  is the tensor of the **direct dipolar interaction** between the nucleus  $i$  and the spin  $\mathbf{S}_v$  of an *unpaired electron*  $v$ .

$$H_F = \mathbf{I}_i \cdot \mathbf{A}_{iv} \cdot \mathbf{S}_v, \quad \text{Hyperfine couplings term (with free electrons)}$$

$A_{iv}$  is the **hyperfine coupling tensor** due to the *contact (Fermi) interaction* between the nucleus  $i$  and an *unpaired electron*  $v$ .

$$H_J = \mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j, \quad \text{Indirect couplings term}$$

$J_{ij}$  is the **indirect coupling tensor** arising from the *Fermi contact* between the nuclei  $i, j$  and the shared *chemical bond electrons*.

$$H_Q = \mathbf{I}_i \cdot \mathbf{Q}_i \cdot \mathbf{I}_i, \quad \text{Quadrupole interactions term}$$

$Q_i$  is the tensor describing the coupling between a *local molecular electric field gradient* and the *electric quadrupole moment* of the nucleus  $i$ .

# The organic chemist's liquid-state Hamiltonian

Most molecules of interest to an organic chemist

- are diamagnetic (have no unpaired electrons),
- have (mostly) just nuclei with spin  $\frac{1}{2}$  (no quadrupole moments),
- 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 parts.

How does the Spin Hamiltonian reduce under these conditions?

# The organic chemist's liquid-state Hamiltonian

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

$$\mathbf{H}_Z = -\hbar\gamma_i \mathbf{B} \cdot \mathbf{I}_i, \quad \text{Zeeman term}$$

Considered as a constant offset. De-facto removed by spectral referencing.

$$\mathbf{H}_{SR} = \mathbf{M} \cdot \mathbf{R}_i \cdot \mathbf{I}_i, \quad \text{Spin-rotation term}$$

Averages to zero under fast tumbling

$$\mathbf{H}_C = \mathbf{B} \cdot \mathbf{C}_i \cdot \mathbf{I}_i, \quad \text{Chemical shifts (screening) term}$$

All tensors reduce to scalars (chemical shifts)

$$\mathbf{H}_{DD} = \mathbf{I}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{I}_j, \quad \text{Direct dipole-dipole interactions term}$$

Averages to zero under fast tumbling

$$\mathbf{H}_{DE} = \mathbf{I}_i \cdot \mathbf{E}_{ij} \cdot \mathbf{S}_v, \quad \text{Dtto between nuclei and free electrons}$$

Absent (no free electrons)

$$\mathbf{H}_F = \mathbf{I}_i \cdot \mathbf{A}_{iv} \cdot \mathbf{S}_v, \quad \text{Hyperfine couplings term (with free electrons)}$$

Absent (no free electrons)

$$\mathbf{H}_J = \mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j, \quad \text{Indirect couplings term}$$

All tensors reduce to scalars (J couplings)

$$\mathbf{H}_Q = \mathbf{I}_i \cdot \mathbf{Q}_i \cdot \mathbf{I}_i, \quad \text{Quadrupole interactions term}$$

Averages to zero under fast tumbling

# The organic chemist's Hamiltonian 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:

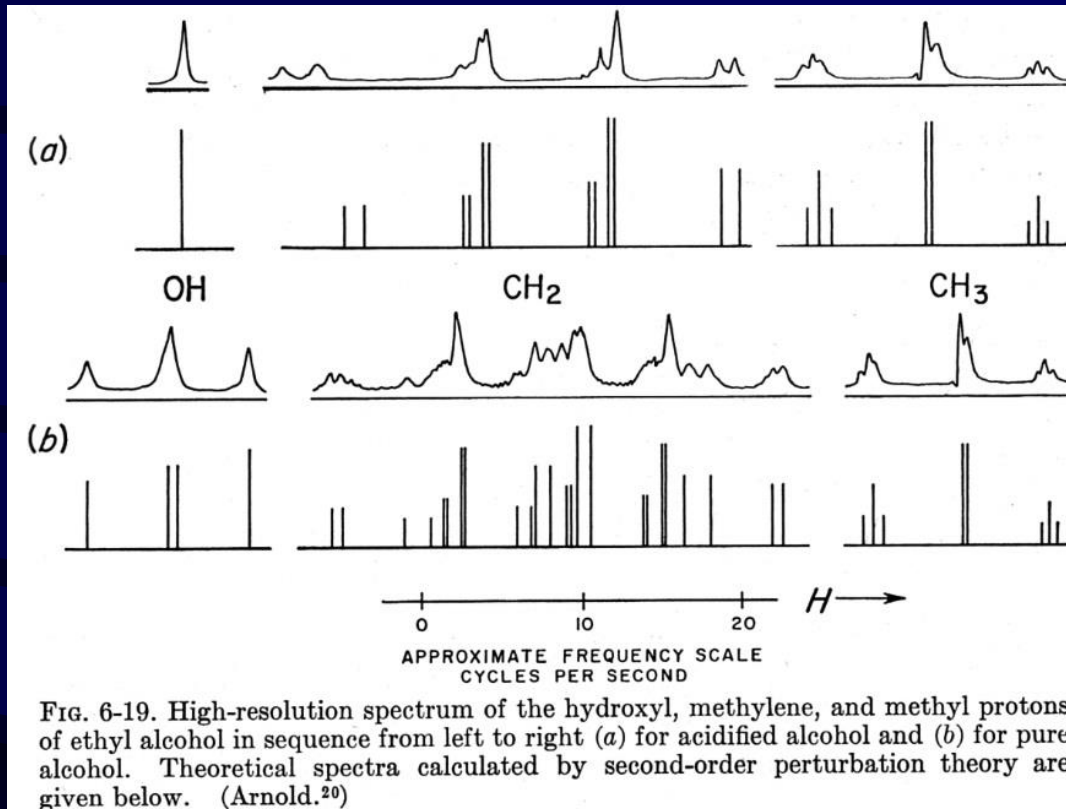
for 3 nuclei: max 3 shifts, 3  $J$ 's; for 10 nuclei: max 10 shifts, 45  $J$ 's

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.

For a given  $n$ , the pattern of missing  $J$ 's defines the spin system type.

# History of the elucidation of the Hamiltonian:

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



30 MHz spectrum, but with a linewidth below 0.2 Hz !!!

To fix the form of terms like J-couplings, first order spectra would have been inadequate. Low, but very homogeneous fields, were better !

## **Special systems and their Hamiltonians**

You can imagine that there are many special systems depending upon the sample aggregation state, chemical composition, the nuclei involved, etc.

## **Experimental ways to affect the Hamiltonian**

Likewise, there are manifold ways to actively affect the Hamiltonian, for example by RF irradiation (decoupling), sample spinning (MAS), and pulse sequences (HOHAHA).

**In all such cases, the Spin Hamiltonian is central!**



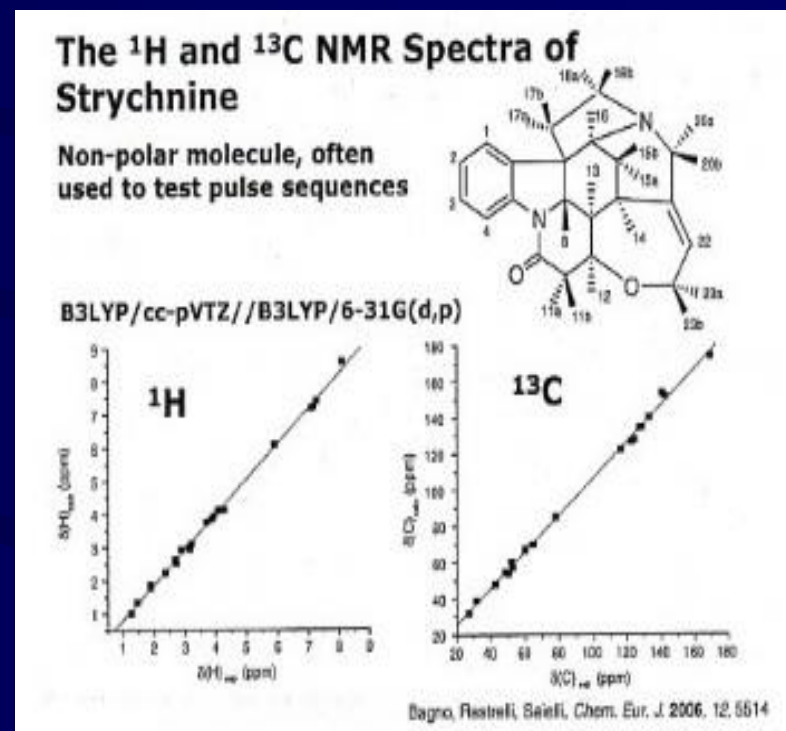
## **II. From Spin Hamiltonian to Spectra**

# Where can one get the spin-system parameters to simulate a spectrum of a give molecule?

Initially, chemical shifts and coupling constants derived from spectra were painstakingly tabulated. From these data eventually emerged empirical rules that permitted to estimate the parameters for new structures, though with errors up to 1 ppm for  $^1\text{H}$ .

With the advent and refinement of Density Function Theory (DFT, 1990's) it became possible to compute the parameters from first principles with pretty good accuracy (ca 0.2 ppm for  $^1\text{H}$ , but with occasional much larger errors and/or inversions).

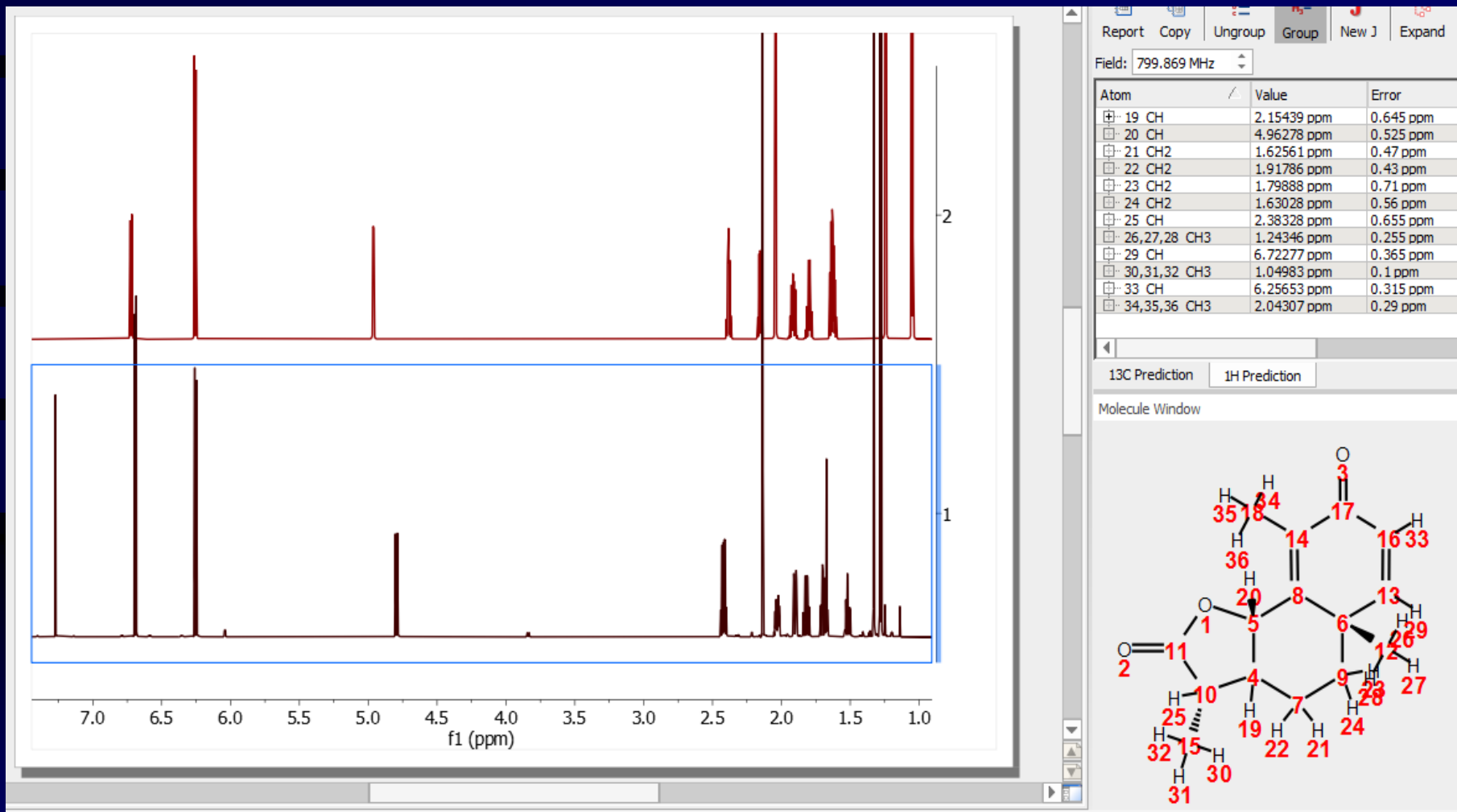
Current work focuses on reducing the wings of the statistical error distributions, while narrowing its central part is of little importance since in practice variations of about 0.2 ppm are in the range of solvent, temperature, and pH effects.



Current practically used approaches try and combine all prediction avenues!

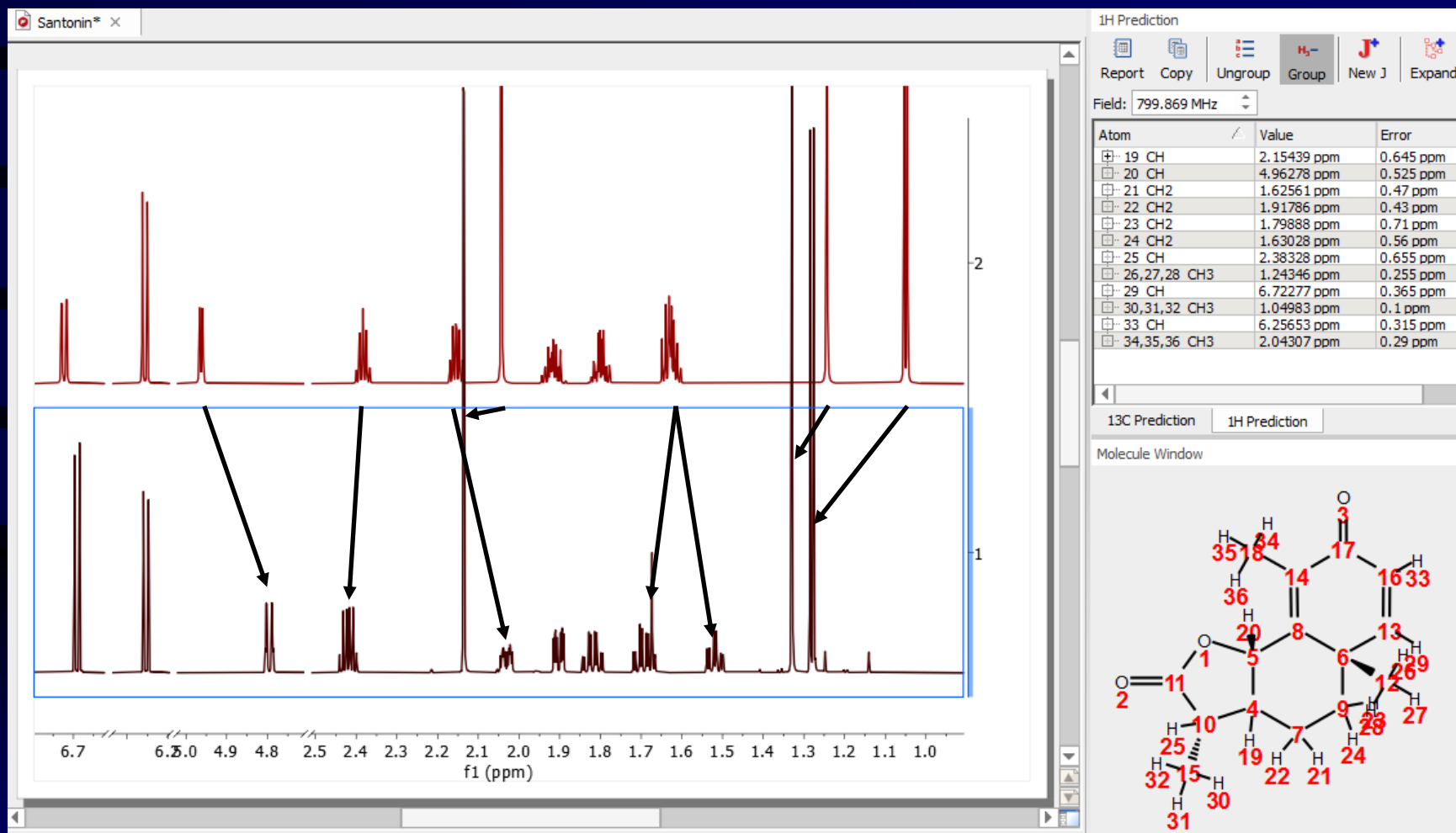
# An example of present-day fast prediction results

Spectrum 1: Experimental spectrum of Santonin at 800 MHz. Spectrum 2: Simulated spectrum



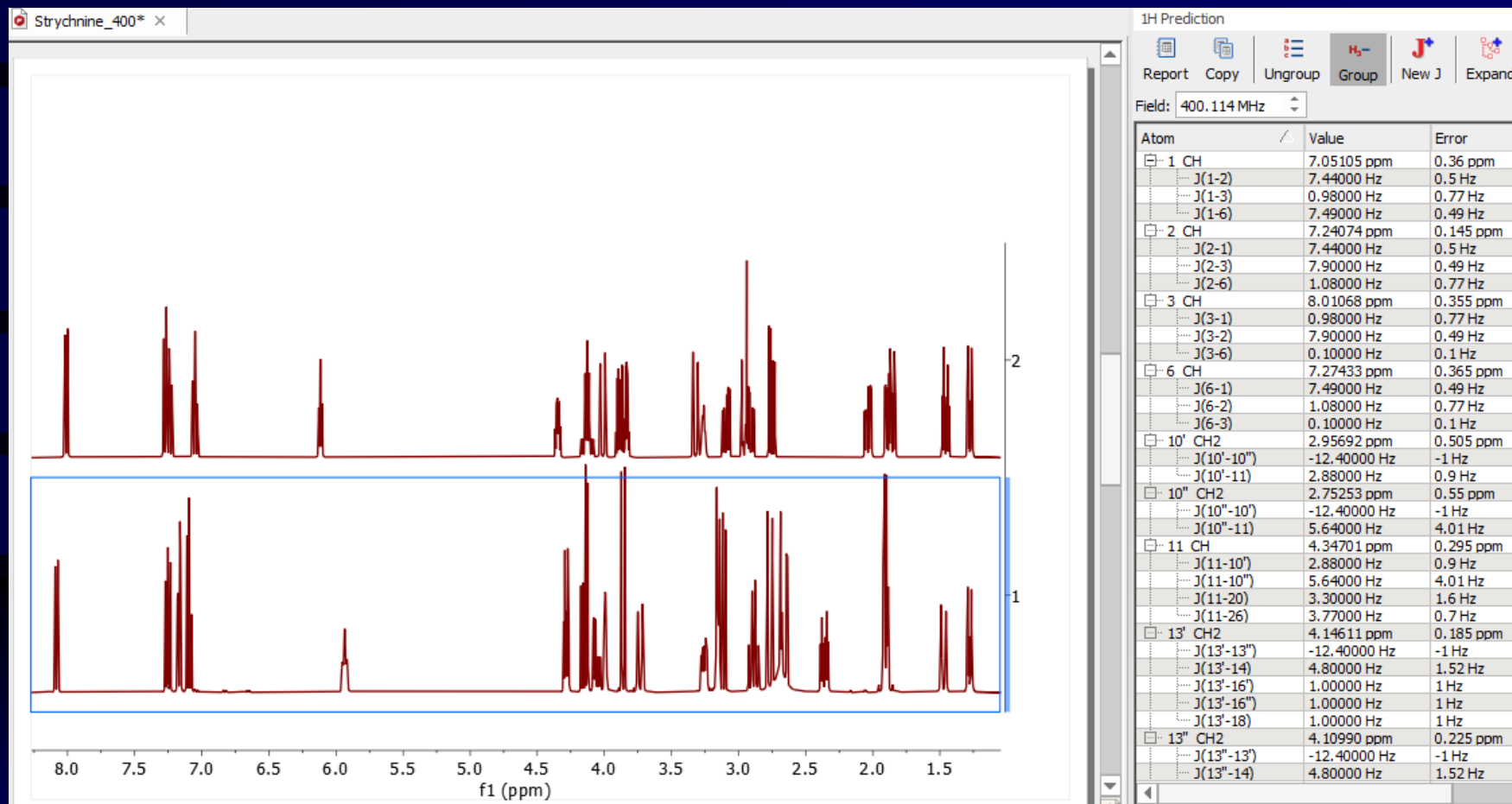
# An example of present-day prediction results: details

Spectrum 1: Experimental data for Santonin at 800 MHz. Spectrum 2: Simulated spectrum



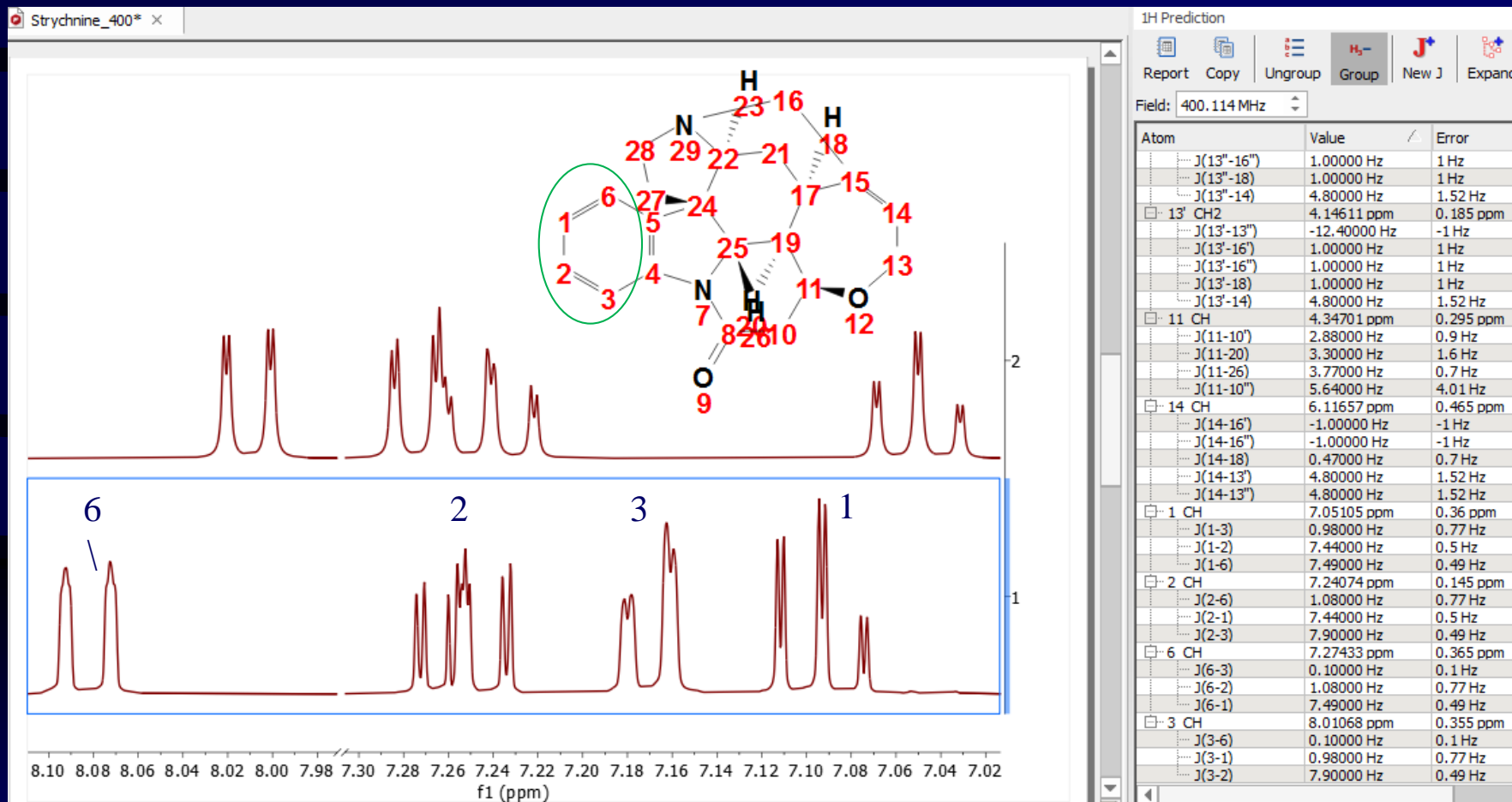
# An example of present-day fast prediction results

Spectrum 1: Experimental spectrum of Strychnin at 400 MHz. Spectrum 2: Simulated spectrum



# An example of present-day fast prediction results: detail

Spectrum 1: Experimental spectrum of Strychnin at 400 MHz. Spectrum 2: Simulated spectrum



*Forward* simulations of NMR spectra  
*rigorous* solutions of *static* cases

## Base spin states of the Spin Hamiltonian

1) 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  $m = +1/2$

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

3) 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:

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

Notes:

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 the total dimension of the corresponding Spin-Hamiltonian matrix.



# Base spin states of the Spin Hamiltonian

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

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

# The matrix form of the Spin Hamiltonian

It is very easy to define 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. A still more stringent rule says that  $H_{K,L} \neq 0$  only if  $|K\rangle$  and  $|L\rangle$  differ in exactly two “digits”; if that happens for digits  $i$  and  $j$ , then  $H_{K,L} = J_{ij}/2$ .
2. When  $K \equiv L$  (diagonal terms),  $H_{K,K}$  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 for nuclei  $i,j$  in  $|K\rangle$  match or  $+1/4$  if they don't 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								

$(101|H|011) = J_{AB}/2$   
 $(101|H|101) = (s_A - s_B + s_C)/2 + (-J_{AB} + J_{AC} - J_{BC})/4$

# Eigenvalues and eigenvectors of the Spin Hamiltonian:

The eigenstates are obtained by diagonalizing the Spin-Hamiltonian matrix  
(obviously 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:  $|(U_a | S^+ | U_b)|^2$

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

# Eureka! A spectrum, finally!

A spectrum is simply the superposition of all spectral transitions

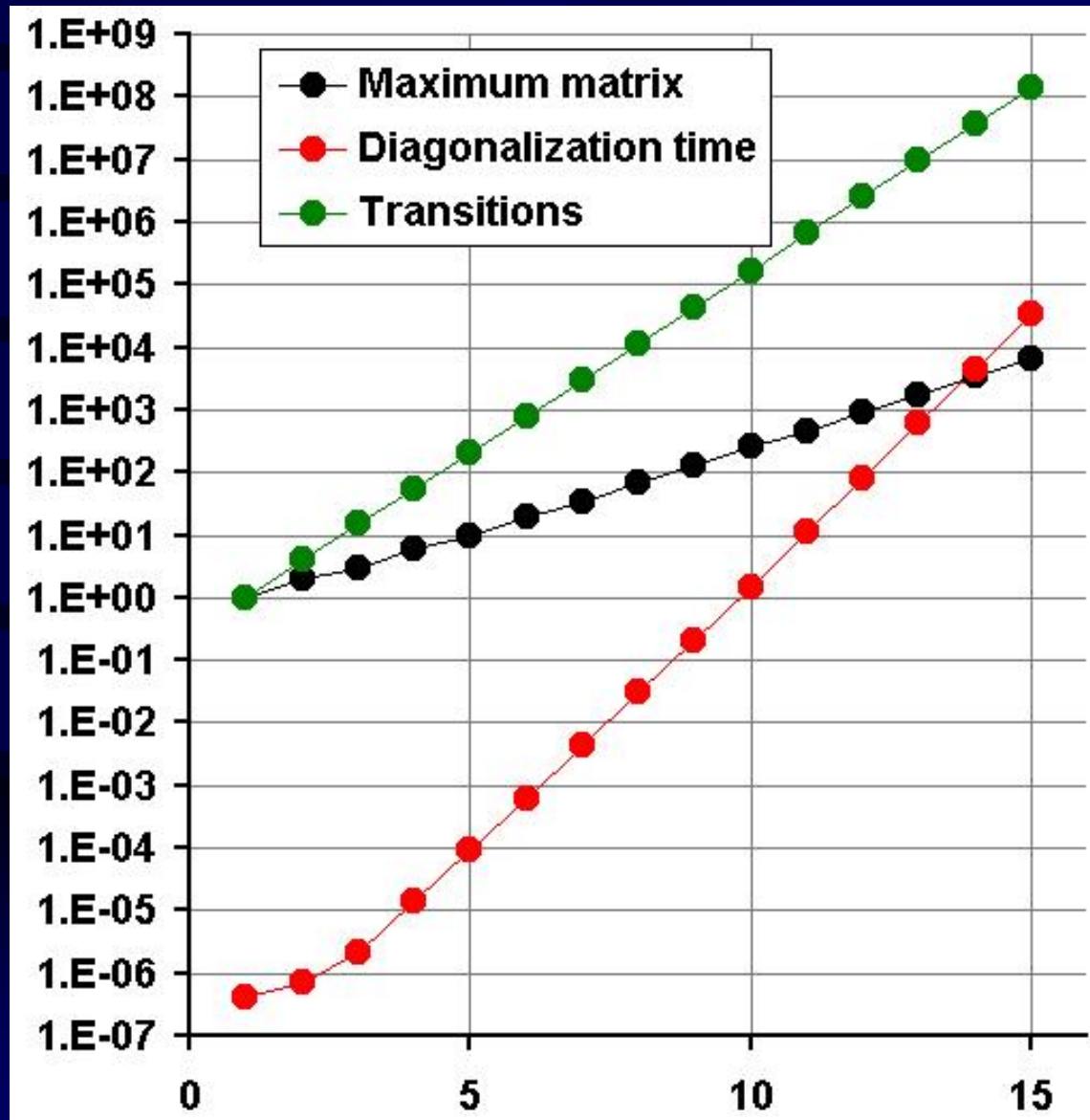
- Transitions compose peaks,
- Peaks group into multiplets,
- Multiplets compose a spectrum

Cool, isn't it!

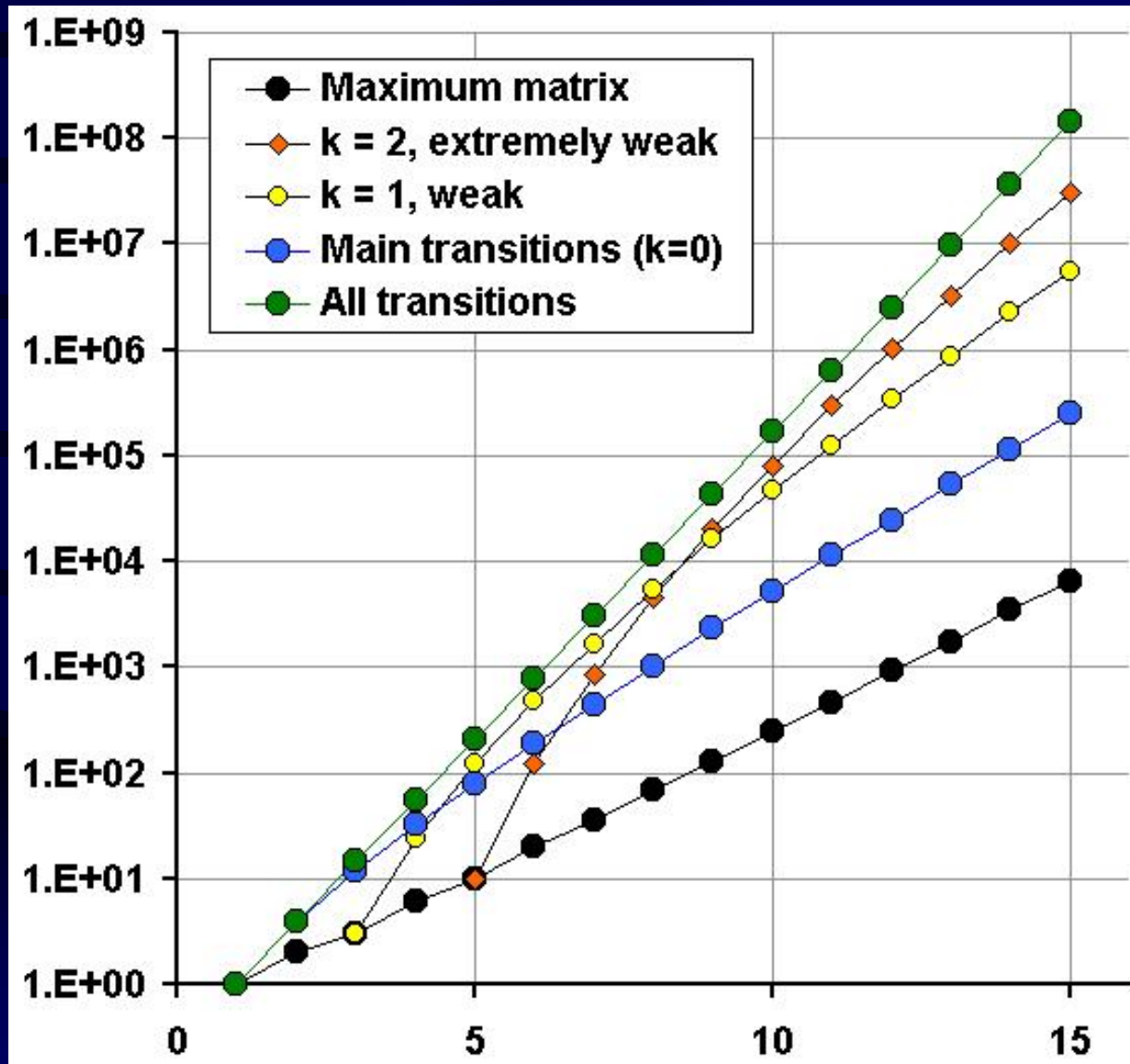
Well ....? Here enters

**the overwhelming combinatorial complexity**

# Simulating spectra and doing it in earnest



# Simulating spectra: counting transitions





# Complexity of the full quantum-mechanical job for N distinct spin-1/2 nuclides

<b>N</b>	<b>Max.Matrix</b>	<b>Diag.Time[sec]</b>	<b>Transitions</b>
2	2	0.00000070	4
3	3	0.0000022	15
4	6	0.000014	56
5	10	0.000090	210
6	20	0.00061	792
7	35	0.0042	3003
8	70	0.030	11440
9	126	0.21	43758
10	252	1.5	167960
11	462	11.	646646
12	924	82.	2496144
13	1716	610.	9657700
14	3432	4500.	37472160
15	6435	34000.	145422675

## Some implications of the combinatorial complexity

Counting the main transitions in molecules we have:

**N = 15: 245'760**

**N = 30: 16'106'127'360**

**N = 45: 791'648'371'998'720**

But in a typical spectrum of such molecules we rarely distinguish more than 200 peaks. For  $N = 30$ , that makes it well over 1000 quantum transitions per resolved peak!

What we see is an envelope of a distribution of Lorentzians

The IV<sup>th</sup> Law of Data Evaluation:

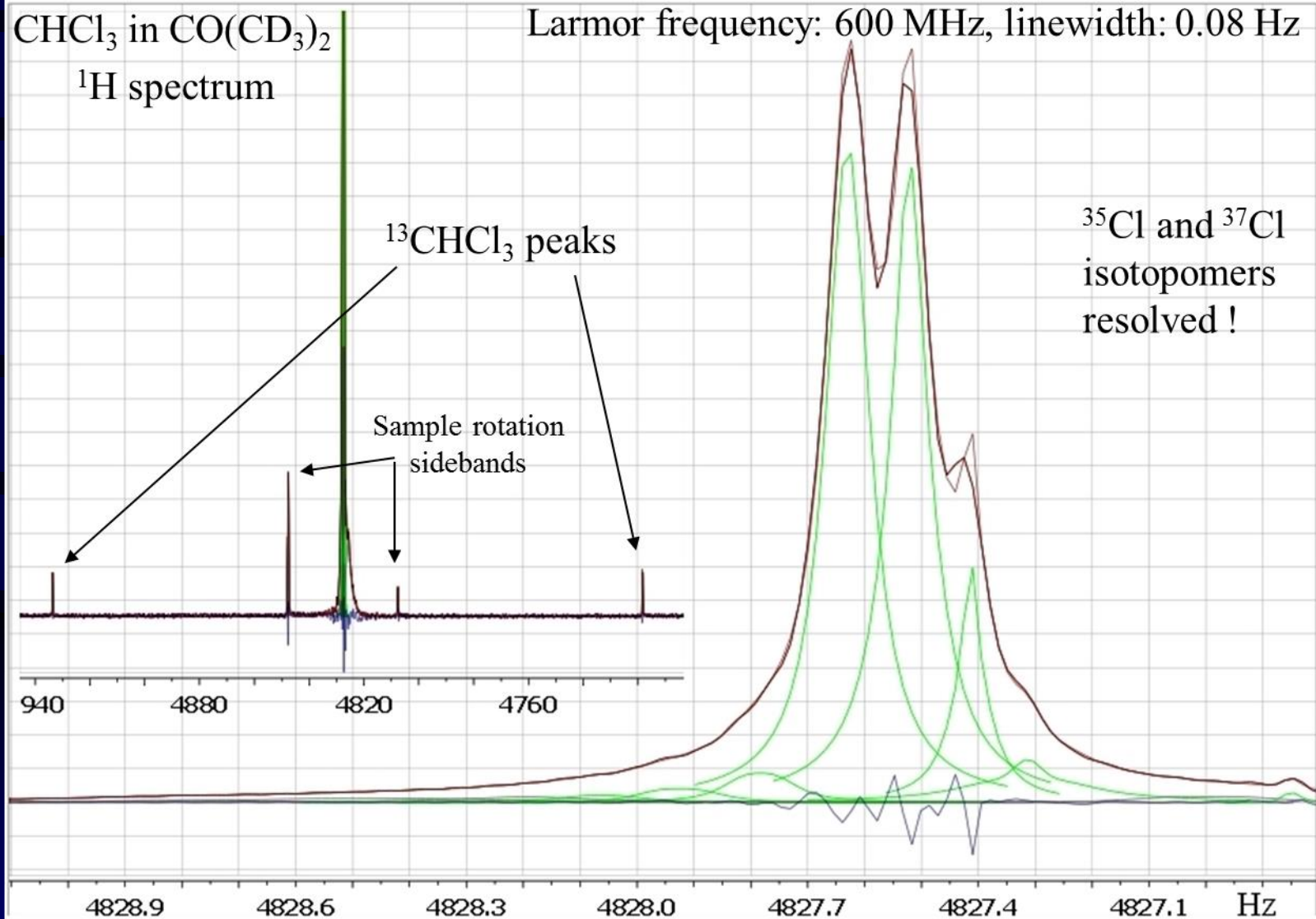
**Don't loose time trying to beat combinatorics!**

**It's hopeless! Can't be done!**

# Sources of peak-shape deviations from the Lorentzian

1. Magnetic field inhomogeneity (shimming)
2. Magnetic field noise ([ebyte.it/library/docs/nmr06a/NMR\\_FieldNoise\\_Fid.html](http://ebyte.it/library/docs/nmr06a/NMR_FieldNoise_Fid.html))
3. Sample spinning (dtt0)
4. Sample temperature gradients (up to 0.01 ppm/deg)
5. FID weighting before FT (Voight and other profiles)
6. Distorsions due to Discrete Fourier Transform (cyclic condition)
7. Overlap of miriads of transitions in coupled spin systems
8. Relaxation effects (e.g., methyl lines contain 3 transitions of different widths)
9. Molecular dynamics effects (chemical exchange, limited mobility)
10. etc ...

# Boosting the spectral resolution would hardly help:



## Other ways to break the impasse

1. Exploiting molecular symmetry ...
2. ... especially full magnetic equivalence ( $A_2, A_3, \dots$ )
3. Fragmentation of the spin system
4. Handling small  $J$ 's a-posteriori by perturbation theory
5. Direct simulation of FID's with interactions time-slicing
6. Approximate methods with acceptable errors ( $\sim 0.01$  Hz)
7. etc. ???

# **Thank you** for your **Attention**

During the whole meeting,  
if you wish to discuss any of these things,  
or any Science in general,  
I have officially pledged to be available

...