

# Measurements of spin diffusion in a homogeneous solid via NMR

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.. it is those laws, which we call the laws of nature...these therefore we must not seek from uncertain conjectures, but learn them from observations and experiments...  
(Sir Isaac Newton).

# Outline

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- Problem statement
- The spin system
- Controlling a many body quantum spin system in NMR
  - Average Hamiltonian Theory
  - Examples from NMR: Hahn echo & ‘magic echo’
- Spin diffusion on a lattice
- Experimental protocol
- Discussion of experimental results
- Conclusions

# Problem statement

Wish to explore how spin diffusion evolves a well-defined microscopic property (a spin state) in the long-time, many-body limit.

# The spin system used in this study: single crystal of calcium fluoride



Image taken from  
<http://www.indiamart.com>

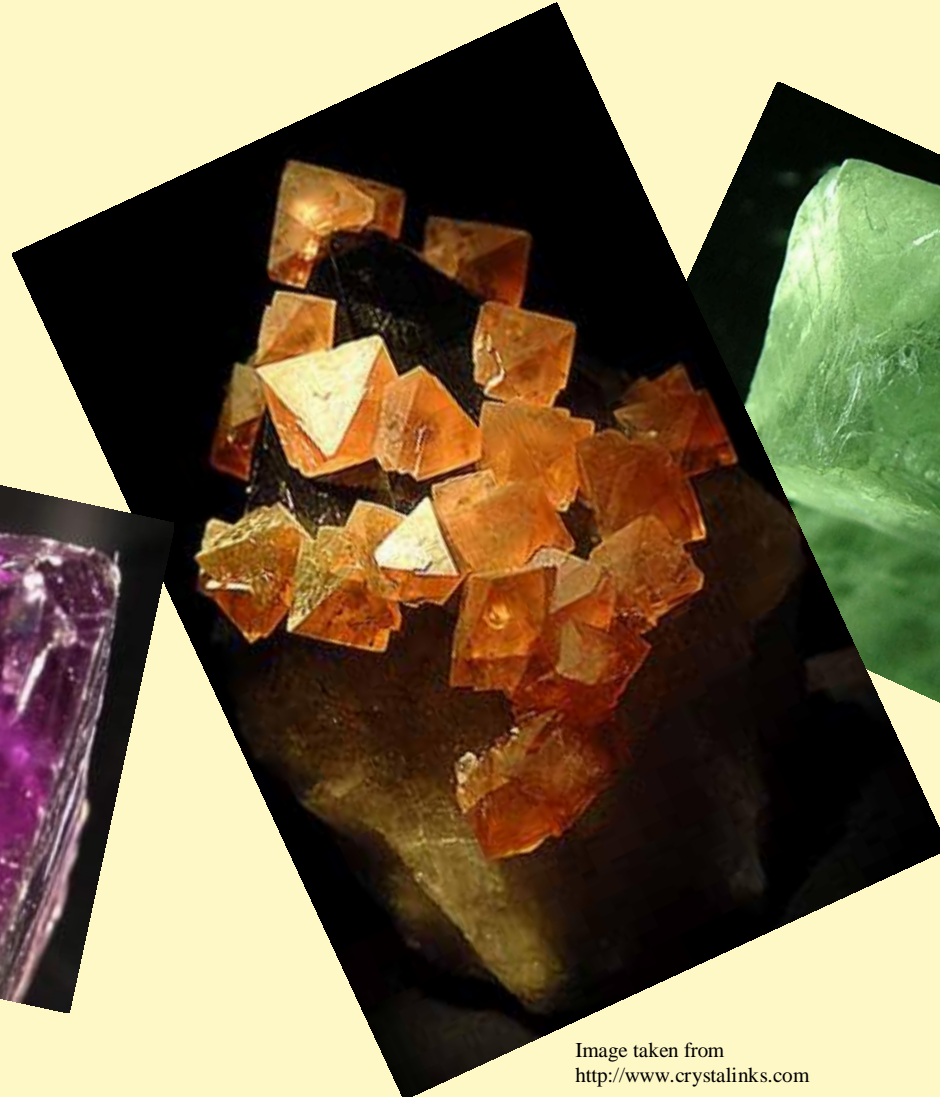


Image taken from  
<http://www.crystalinks.com>

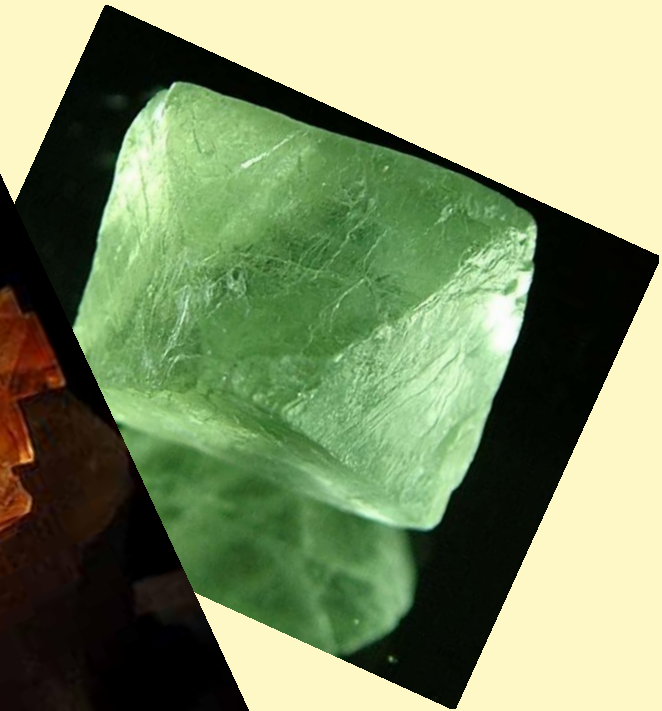


Image taken from  
<http://www.gemrockauctions.com>

# About the spin system

- $^{19}\text{F}$  nuclear spins are coupled by a dipolar interaction which in a strong magnetic field ( $H_Z \gg H_D$ ) is given by

$$H_D = \frac{1}{4} \sum_{i < j}^N \gamma^2 \hbar^2 \frac{(1 - 3 \cos^2 \vartheta_{ij})}{r_{ij}^3} [ 2I_z^i I_z^j - \frac{1}{2} \{ I_+^i I_-^j + I_-^i I_+^j \} ]$$

- Sparse paramagnetic impurities: **irreversible** processes
- Wish to explore how the highlighted term evolves a well-defined microscopic property (a spin state) in the macroscopic limit.

# The dynamics of the flip-flop interaction: spin diffusion

$$H_{ff} = \frac{1}{2} \sum_{i < j}^N b_{ij} [I_+^i I_-^j + I_-^i I_+^j]$$
$$b_{ij} = \frac{1}{4} \gamma^2 \hbar^2 \frac{(1 - 3 \cos^2 \theta_{ij})}{r_{ij}^3}$$

An example: Can spatially propagate the state of one spin, to a dipolar coupled neighbor

$$E_+^i \otimes 1^j \xrightarrow{H_{ff}} 1^i \otimes E_+^j$$

where

$$E_+^i = (1 + 2I_z^i) / 2$$

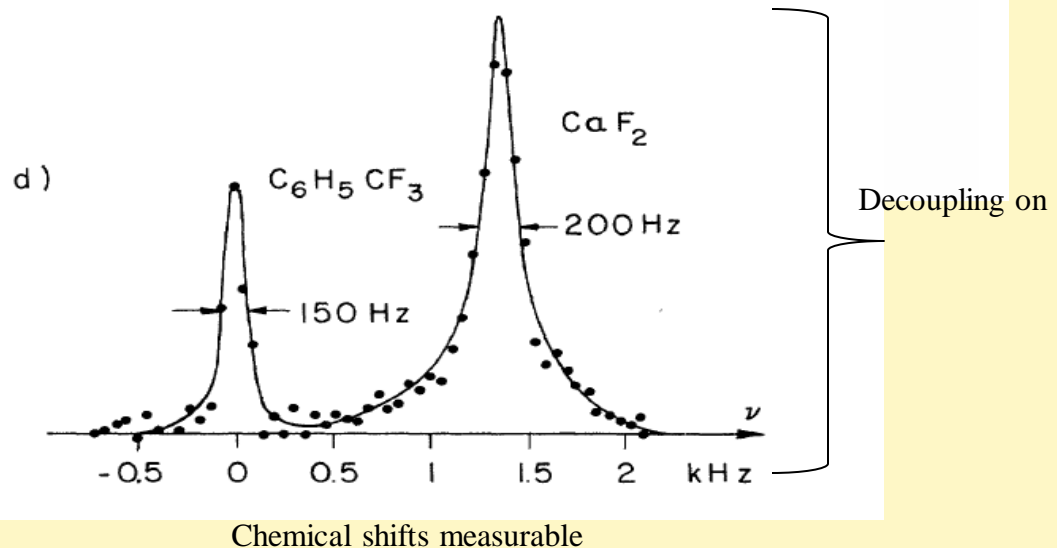
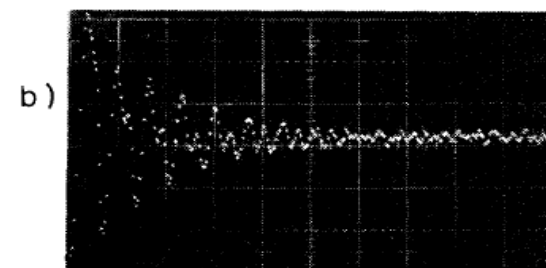
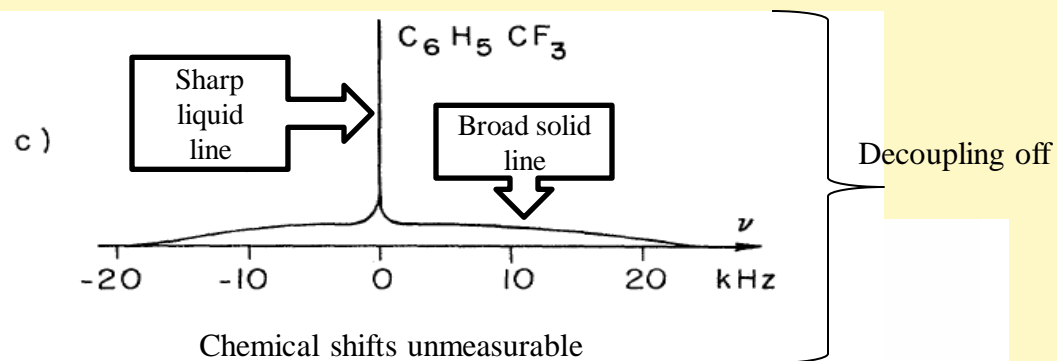
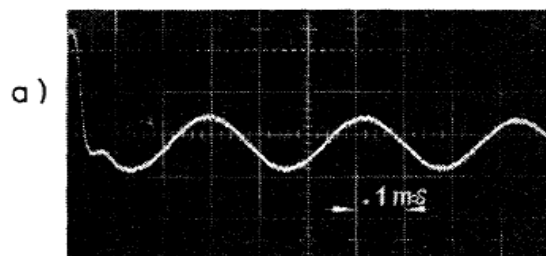
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# Average Hamiltonian Theory



A celebrated example (WAHUHA sequence) demonstrating the ability to effectively turn off the strong nuclear dipolar interaction allowing for the measurement of the (much weaker) chemical shift interaction

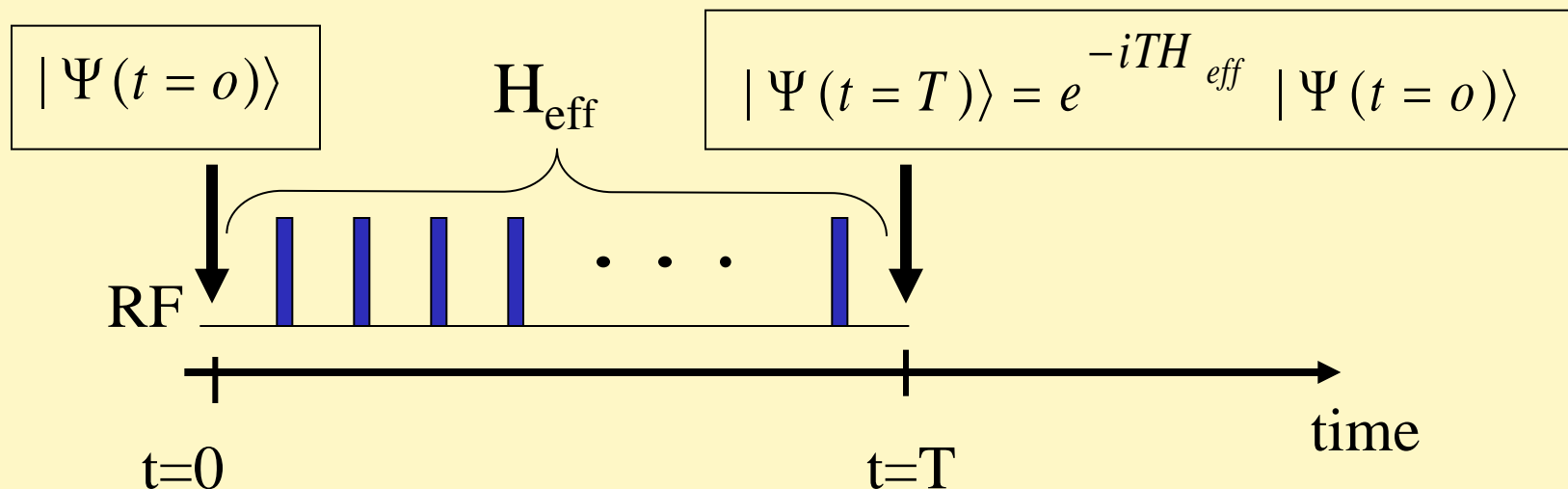


# Average Hamiltonian Theory

- A well known and established method for controlling how a system evolves under a desired effective Hamiltonian by manipulating the dynamics with an experimentally controllable time dependent Hamiltonian.
- Not tied to Nuclear Magnetic Resonance(NMR), though NMR is a very suitable system for its application and has demonstrated the applicability and great success of the theory through numerous investigations such as in spectroscopy and imaging.

# Average Hamiltonian Theory in NMR

- To replace a sequence of Radio Frequency (RF) pulses (indicated by **■** in the figure) and evolutions under an internal Hamiltonian by a **time independent** effective Hamiltonian,  $H_{\text{eff}}$ , and experimentally implement a desired evolution of the spin system.
- $H_{\text{eff}}$  evolves the system from the state  $|\Psi(t=0)\rangle$  to  $|\Psi(t=T)\rangle$ .



# Overview of Average Hamiltonian Theory

One aspect of the theory involves analyzing the transformation of an interaction ( $H_{\text{int}}$ ) in a frame rotating with the applied RF pulses.

The time evolution of the density matrix is given by

$$\rho(t_c) = U_{RF} U_{\text{int}} \rho(0) U_{\text{int}}^{-1} U_{RF}^{-1}$$

$U_{RF}$  represents the interaction associated with the sequence of RF pulses applied over a time  $t_c$ .

$H_{\text{int}}$  refers to the systems' internal Hamiltonians (chemical shifts, field inhomogeneity, dipolar coupling)

An appealing aspect of the formalism is that a variety of Hamiltonians can be accounted for such as : pulse errors, pulse transients & finite pulse width effects

$$U_{RF} = \dots U_2 U_1 U_0$$

$$U_{\text{int}}(t_c) = \exp[-it_c (\overline{H}_{\text{int}}^0 + \overline{H}_{\text{int}}^1 + \dots)]$$

Dyson Series

$$\overline{H}_{\text{int}}^0 = \frac{1}{t_c} \int_0^{t_c} \tilde{H}_{\text{int}}(\tau) d\tau$$

$$\overline{H}_{\text{int}}^1 = \frac{-i}{2t_c} \int_0^{t_c} [\tilde{H}_{\text{int}}(\tau), \int_0^{\tau} \tilde{H}_{\text{int}}(\phi) d\phi] d\tau$$

$$\overline{H}_{\text{int}}^2 = \dots$$

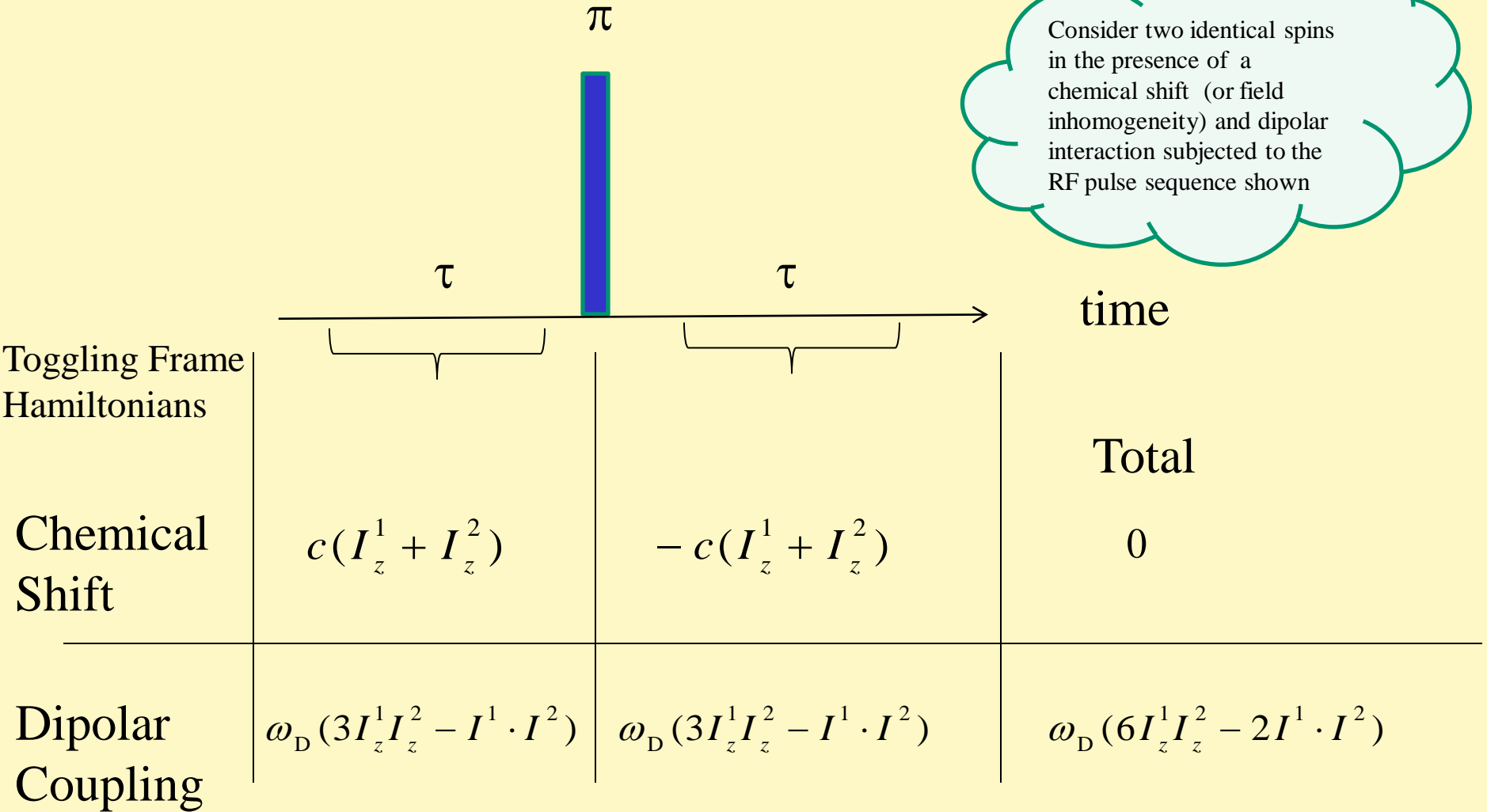
$$\tilde{H}_{\text{int}}(t) = U_{RF}^{-1} H_{\text{int}} U_{RF}$$

Magnus

Expansion

# The Hahn-echo sequence

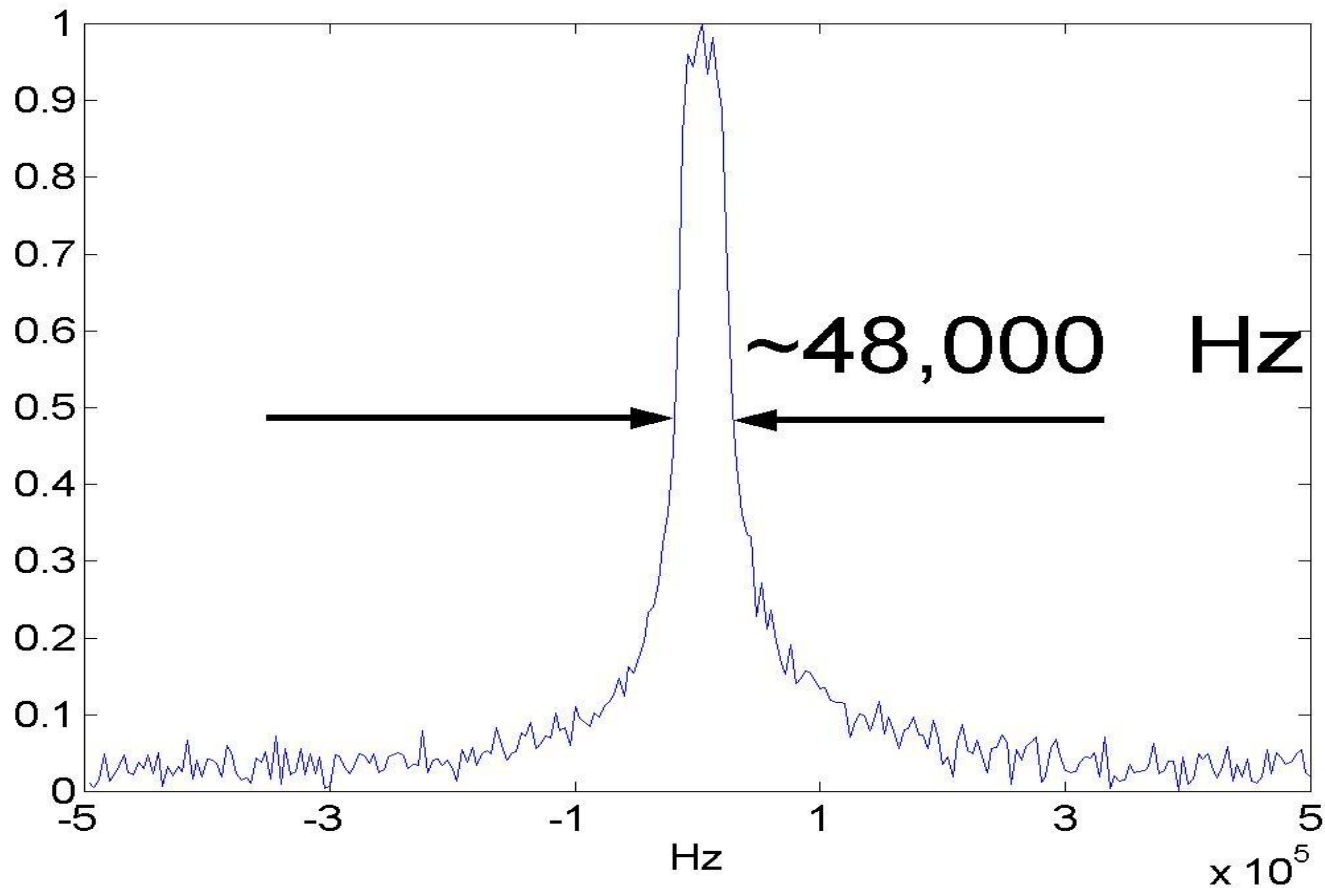
Consider two identical spins in the presence of a chemical shift (or field inhomogeneity) and dipolar interaction subjected to the RF pulse sequence shown



If the system is sampled at interval  $2\tau$  it will appear to have evolved under an effective Hamiltonian which is twice the dipolar interaction. The chemical shift interaction is ‘turned-off’.

# A sample calcium fluoride spectrum

- Without multiple pulse one experimentally observes a broad line-width due to strong dipolar interactions.



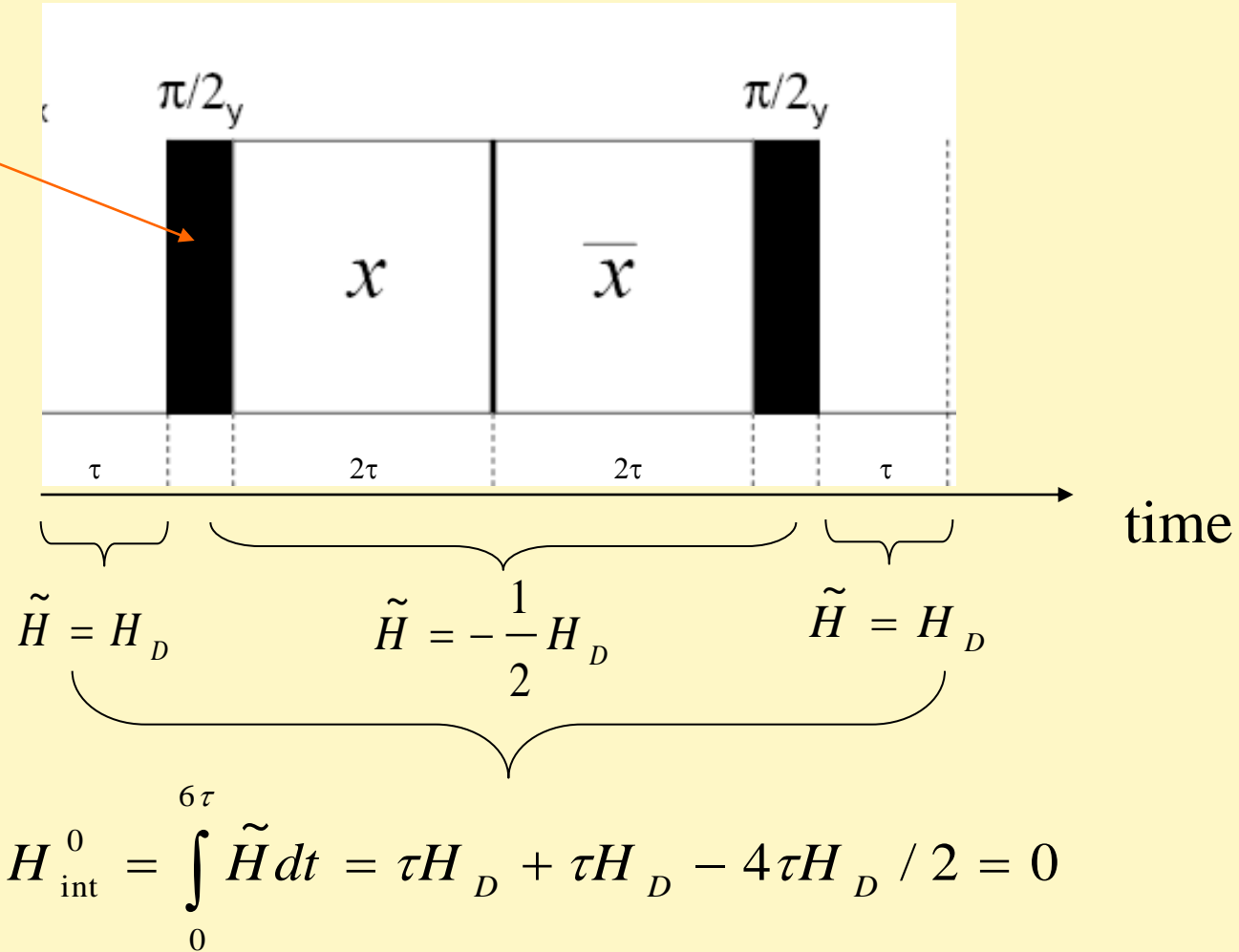
# Using a magic echo to ‘turn off’ the dipolar coupling in our spin system

- Under **perfect experimental conditions**, the cycle time-reverses the evolution of a system of nuclear spins that are coupled by a dipolar Hamiltonian ( $H_D$ ) by a change of sign of the effective Hamiltonian of the sequence.

$$H_{\text{eff}} = -1/2H_D$$

# The Magic Echo Cycle

RF Pulses



Under this cycle the system will appear to not evolve under the dipolar interaction as approximated to zeroth order of the Magnus Expansion.

# Accounting for errors in average Hamiltonian calculation

- $H_{\text{eff}}$  affected by experimental errors

(RF pulse transients, finite pulse widths, pulse errors ...).

$$H_{\text{eff}} = -1/2H_D + \text{errors}$$

- AHT allows one to account for a variety of pulse errors that may plague a multiple pulse cycle by considering their effect on  $H_{\text{eff}}$ , and then design cycles which remove their contribution to perform the desired transformation.
- Considered the effects of finite pulse width in the  $\pi/2$  pulse, pulse flip errors, and symmetric phase transients.



# Removing $H_D$ and correcting for errors(1)

- Can remove the effect of  $H_D$  using a pulse sequence with  $H_{eff} = -H_D$
- The  $\pi/2$  pulse widths are not negligible but easily accounted for in the calculation of  $H_{eff}$ .

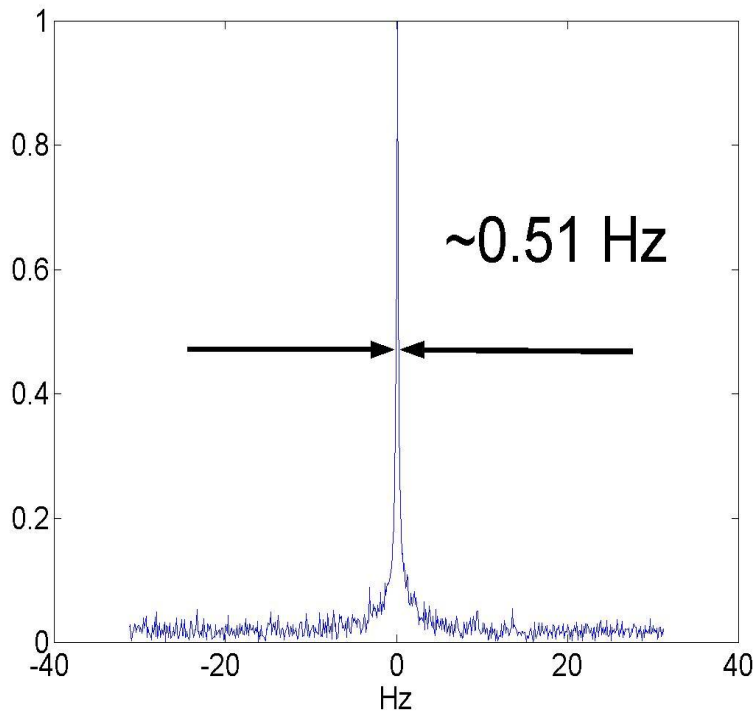
$$H_{eff} = -1/2 H_D + \underbrace{\alpha (I_x^i I_x^j - I_y^i I_y^j)}_{\text{Contribution of Finite pulse widths}}$$

$2\alpha$  is the  $\pi/2$  pulse width

Resulting line narrowing: **361 Hz**

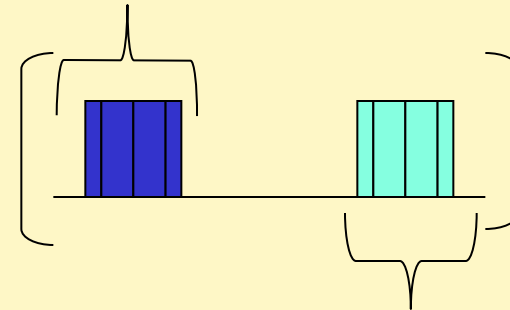
# Removing $H_D$ and correcting for errors (2)

- Can remove the effect of finite pulse widths by alternating the phases of pulses in a well defined way, and then making a measurement over a larger cycle which removes their effect on the spin evolution.



## Simplified pulse sequence diagram

$$H_{eff} = -1/2 H_D + \alpha (I_x^i I_x^j - I_y^i I_y^j)$$



$$H_{eff} = -1/2 H_D - \alpha (I_x^i I_x^j - I_y^i I_y^j)$$

$$H_{eff}(\text{total}) = -H_D$$

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# A single crystal of calcium fluoride

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$$b_{ij} = \frac{1}{4} \gamma^2 \hbar^2 \frac{(1 - 3 \cos^2 \theta_{ij})}{r_{ij}^3}$$

An example: Can spatially propagate the state of one spin, to a dipolar coupled neighbor

$$E_+^i \otimes 1^j \xrightarrow{H_{ff}} 1^i \otimes E_+^j$$

where

$$E_+^i = (1 + 2I_z^i) / 2$$

# Zeeman order

Nuclear spins are aligned along a strong external magnetic field, at room temperature

$$\rho = 1 - \varepsilon \sum_i I_z^i$$

$\varepsilon = \gamma B / kT$   
 $\rho =$  density operator

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# Dipolar order

Nuclear spins are aligned along local dipolar fields of other nuclear spins

$$\rho = 1 - c H_D \quad c \text{ is constant}$$

In a strong external magnetic field the dipolar ordered state scales as  $H_D$ .

# A toy model of spin diffusion

Purpose of the model

- a. Highlight the method of measurement
- b. Highlight the dynamics of spin-diffusion
- c. Do **NOT** want to calculate a diffusion rate

# Follow the evolution for a single polarized spin

$$\rho(o) = 1 - \varepsilon E_+^j \otimes 1^k \otimes 1^l \otimes 1^m \dots$$



State preparation: +gradients,  $H_D = 0$

$$\rho(o) = 1 - \left( e^{i\varphi_j} \right) E_+^j \otimes 1^k \otimes 1^l \otimes 1^m \dots$$

$$\varphi_j = kz_j$$

$$k = \gamma \frac{\partial B_z}{\partial z} t$$



Evolution: under  $H_D$  for a variable time 'τ'.

$$\rho(\tau) = 1 - \left( e^{i\varphi_j} \right) 1^j \otimes 1^k \otimes E_+^l \otimes 1^m \dots$$



Readout: -gradients,  $H_D = 0$

$$\rho(\tau) = 1 - \left( e^{i\varphi_j} e^{-i\varphi_l} \right) 1^j \otimes 1^k \otimes E_+^l \otimes 1^m \dots$$



•In general

$$\rho(\tau) = 1 - \varepsilon \sum_k c_k I_z^k e^{i(\varphi_j - \varphi_k)} = 1 - \varepsilon \sum_k c_k I_z^k e^{i\Delta\varphi_{jk}}$$

•The detected signal  $\langle I_z \rangle = \text{Tr} [\rho I_z]$

$$\langle I_z \rangle = \varepsilon \left\langle \sum_k c_k e^{i\Delta\varphi_{jk}} \right\rangle = \varepsilon \left\langle 1 - \frac{(\Delta\varphi)^2}{2} + \dots \right\rangle$$

•Long time many spin limit

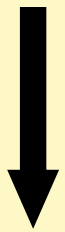
- $\Delta\varphi$  small and random

-spread of the phase behaves diffusively

$$\langle (\Delta\varphi)^2 \rangle / 2 = k^2 \langle (\Delta z)^2 \rangle / 2 = k^2 D\tau$$

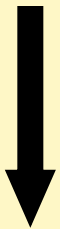
# Spin diffusion of dipolar order

$$\rho(0) = 1 - \epsilon \left( e^{i\varphi_j} \right) E_+^j \otimes 1^k \otimes 1^l \otimes 1^m \dots$$



Create dipolar order

$$\rho(0) = 1 - \epsilon c e^{i\varphi_j} \left( 3 I_z^j I_z^k - I^j \cdot I^k \right) \otimes 1^l \otimes 1^m \otimes 1^n \dots$$



Evolution under  $H_D$  for a variable time 'τ'

$$\rho(\tau) = 1 - \epsilon c \left( e^{i\varphi_j} \right) 1^j \otimes 1^k \otimes \left( 3 I_z^l I_z^m - I^l \cdot I^m \right) \otimes 1^n \dots$$

# Spin diffusion of dipolar order

$$\rho(\tau) = 1 - \varepsilon c (e^{i\varphi_j}) 1^j \otimes 1^k \otimes (3I_z^l I_z^m - I^l \cdot I^m) \otimes 1^n \dots$$

↓ Convert back to Zeeman order for detection

$$\rho(\tau) = 1 - \varepsilon \left[ \begin{array}{l} w_l (e^{i\varphi_j}) 1^j \otimes 1^k \otimes I_z^l \otimes 1^m \dots \\ + w_m (e^{i\varphi_j}) 1^j \otimes 1^k \otimes 1^l \otimes I_z^m \dots \end{array} \right]$$

↓ Readout: -gradients,  $H_D = 0$

$$\rho_{readout}(\tau) = 1 - \varepsilon \left[ \begin{array}{l} w_l (e^{i(\varphi_j - \varphi_l)}) 1^j \otimes 1^k \otimes I_z^l \otimes 1^m \dots \\ + w_m (e^{i(\varphi_j - \varphi_m)}) 1^j \otimes 1^k \otimes 1^l \otimes I_z^m \dots \end{array} \right]$$

•The detected signal  $\langle I_z \rangle = \text{Tr} [\rho I_z]$

•In general

$$\langle I_z \rangle = \varepsilon \left\langle \sum_l w_l e^{i\Delta\varphi_{jl}} + \sum_m w_m e^{i\Delta\varphi_{jm}} \right\rangle$$

•Long time many spin limit

- $\Delta\varphi$  small and random

-spread of the initial phase behaves diffusively

$$\langle I_z \rangle = \varepsilon \left\langle 1 - (\Delta\varphi)^2 + \dots \right\rangle$$
$$\langle (\Delta\varphi)^2 \rangle = k^2 \langle (\Delta z)^2 \rangle = 2k^2 D\tau$$

$$\langle I_z \rangle_{dipolar} = \varepsilon \left\langle 1 - (\Delta \varphi)^2 + \dots \right\rangle$$

$$\langle I_z \rangle_{Zeeman} = \varepsilon \left\langle 1 - \frac{(\Delta \varphi)^2}{2} + \dots \right\rangle$$

- Model indicates a difference due to spin correlations in case of dipolar order.
- Spin system is actually more complex.

# Outline

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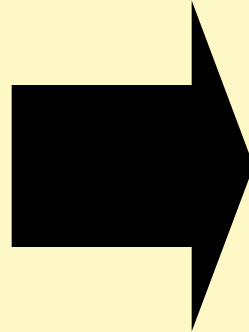
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# Why this experiment is challenging

Spin diffusion rate has been predicted to be very slow:

$$D \sim 1 \times 10^{-12} \text{ cm}^2/\text{s}$$

The displacement of spin coherence is therefore approximately  $1 \mu\text{m}$  in about 1 hour.



The spatially encoded profile needs to have a wavelength on this length scale to probe the dynamics.

Attenuation due to diffusion needs to be larger than that due to relaxation.

Sample sizes are  $\sim 1 \text{ mm}^3$ . The precisions required to encode and then refocus the residual phase encoding is therefore on the order of 1 part in  $10^5$ .

# State preparation

- Encode profile with wavelength on the order of 1 micron
  - Suppress internal dipolar coupling (including spin diffusion and any offset) using average Hamiltonian methods
  - Apply short, strong pulsed gradients in well-defined times of RF pulse sequence.



# Experimental techniques

- Improved a radio-frequency pulse sequence for controlling nuclear spin degrees of freedom by correcting for finite pulse width errors, RF transients, and other pulse errors, to better decouple the nuclear spins.
- Pulsed gradient fields to the sample (Solid state NMR probe with an efficient gradient & RF coil)
- High pulsed currents (25-50 A) for the gradients, in short times (20-30  $\mu\text{s}$ ) & reproducibility must be less than 1 in  $10^5$  (electronic circuitry).

# Design of the gradient coil (schematic does not include RF coil for manipulating spin dynamics)

## Conditions for uniform gradient

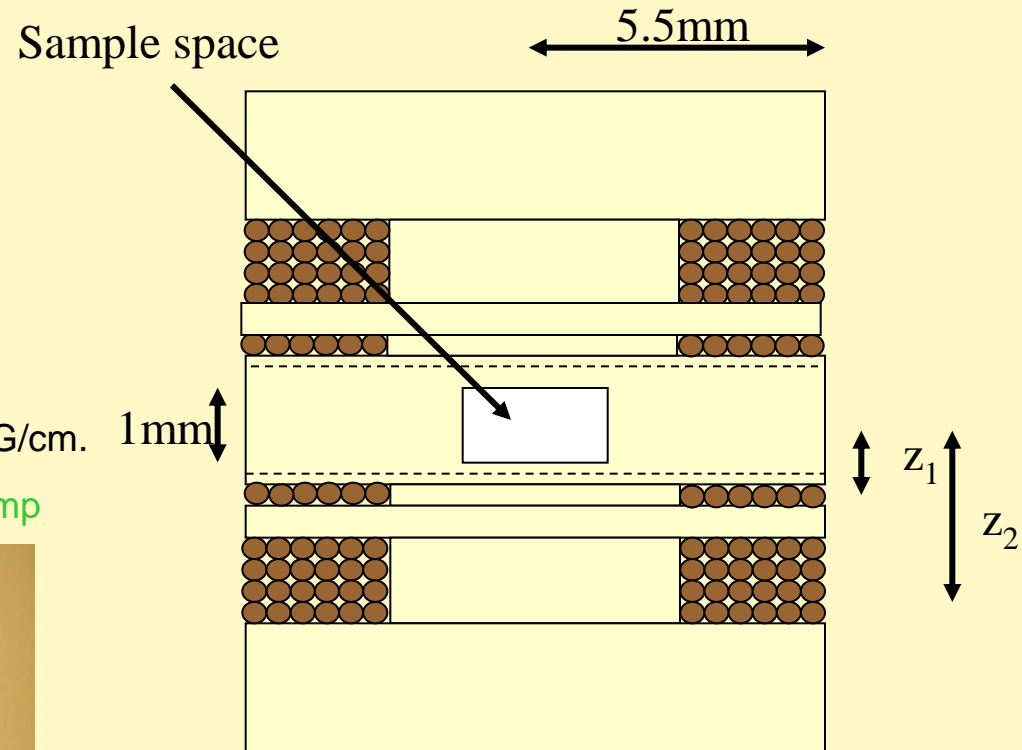
$$z_1 = 0.44R \quad \frac{S_2}{S_1} = 7.47 \quad z_2 = 1.19R$$

## Advantages of this coil configuration

A very strong gradient field can be created

Conventional gradient coils produce ~50 to 100 G/cm.

This gradient coil design ~ 20,000 G/cm @ 55 Amp



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# Experimental results

$D_z$  Diffusion constant of Zeeman order

$D_E$  Diffusion constant of dipolar order

$T_1$  Relaxation time of Zeeman order

$T_{1D}$  Relaxation time of dipolar order

# Experimental Measurements

## Zeeman Diffusion

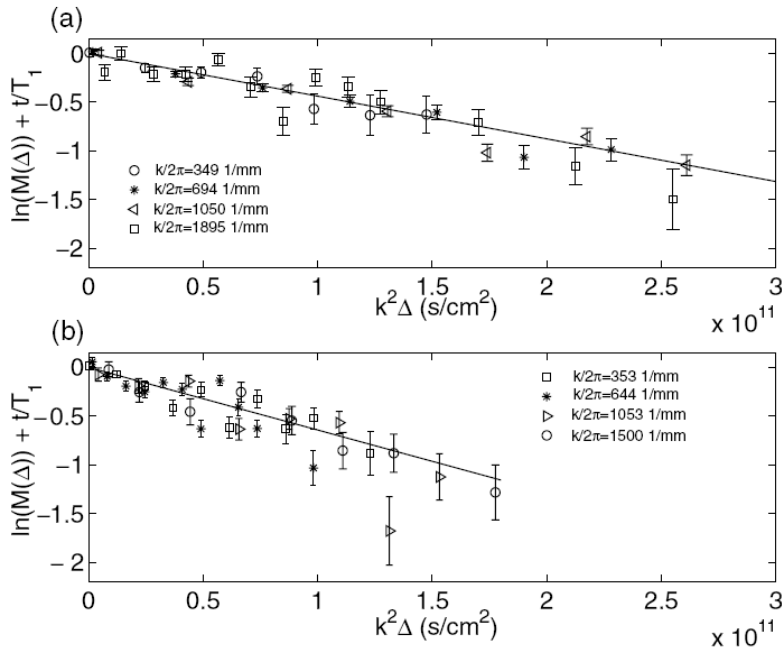


FIG. 2. Experimental results of the spin diffusion rate of Zeeman order with the crystal aligned along (a) the [111] direction—the pulsed gradient fields generated are  $\circ$ , 2886 G/cm;  $*$ , 5661 G/cm;  $\triangleleft$ , 8510 G/cm;  $\square$ , 8510 G/cm; and (b) the [001] direction—the pulsed gradient fields generated are  $\square$ , 2886 G/cm;  $*$ , 5661 G/cm;  $\triangleright$ , 8695 G/cm;  $\circ$ , 7474 G/cm. The error in  $k$  is approximately 3%.

## Dipolar Diffusion

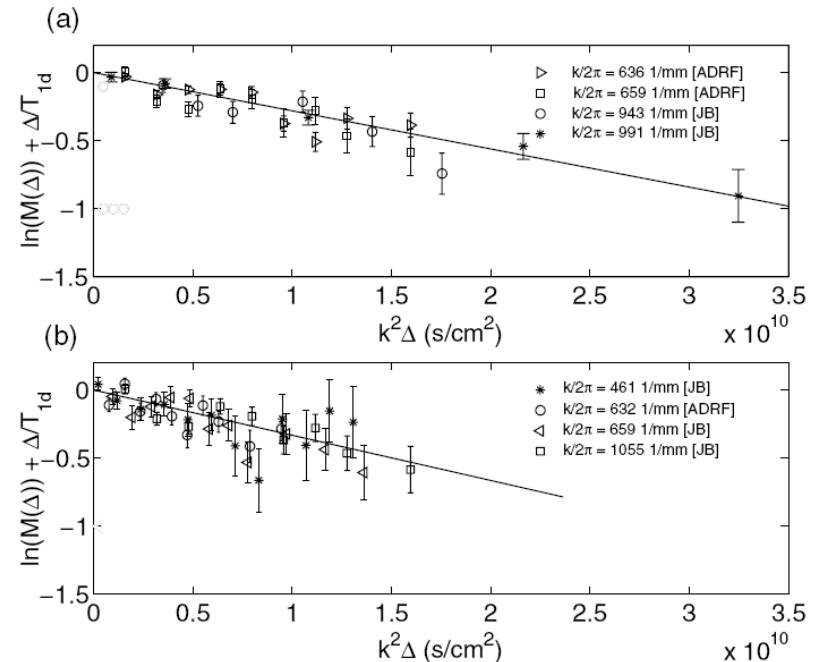


FIG. 3. Experimental results of the spin diffusion rate of dipolar order with the crystal aligned along (a) the [001] direction—the pulsed gradient fields generated are  $\triangleright$ , 5698 G/cm;  $\square$ , 5698 G/cm;  $\circ$ , 8473 G/cm;  $*$ , 8399 G/cm; and (b) the [111] direction—the pulsed gradient fields generated are  $*$ , 2886 G/cm;  $\circ$ , 8436 G/cm;  $\triangleleft$ , 5661 G/cm;  $\square$ , 8362 G/cm. The error in  $k$  is approximately 3%.

# Summary of the experimental results for the diffusion rates of Zeeman and dipolar order

Measurements performed in this study	[001]	[111]
$D_E$ [ $\times 10^{-12}$ cm <sup>2</sup> /s]	$29 \pm 3$	$33 \pm 4$
$D_Z$ [ $\times 10^{-12}$ cm <sup>2</sup> /s]	$6.4 \pm 0.9$	$4.4 \pm 0.5$
$T_1$ [s]	$256.2 \pm 3.4$	$287.5 \pm 7.0$
$T_{1D}$ [s]	$9.1 \pm 0.1$	$9.0 \pm 0.2$

# Zeeman order: Comparison with theory & simulation

Theoretical studies of $D_z$	$D_z[001]$ $\times 10^{-12}$ [cm <sup>2</sup> /s]	$D_z[111]$ $\times 10^{-12}$ [cm <sup>2</sup> /s]	$\frac{D_z[001]}{D_z[111]}$
Moment Calculation (Redfield and Yu)	8.22	6.71	1.22
Irreversible Statistical Mechanics (Borckmans and Walgraef)	6.98	4.98	1.40
Simulation of classical gyro-magnets (Tang and Waugh)	7.43	No data	No data
Hydrodynamic Approach (D. Greenbaum et. al. )	8.1	7.4	1.1

Experimental Measurement:  $\frac{D_z[001]}{D_z[111]} = 1.4 \pm 0.2$

- 
- G.S. Boutis, D. Greenbaum, H. Cho, D. G. Cory, C. Ramanathan "Spin diffusion of correlated two-spin states in a dielectric crystal" (2004) *Phys. Rev. Lett.* 92: 13 137201-137205
- A.G. Redfield, W. N. Yu "Moment-Method Calculation of Magnetization and Interspin-Energy Diffusion" (1968) *Phys. Rev.* 169, 443–450.
- P. Borckmans, D. Walgraef "Irreversibility in Paramagnetic Spin Systems: Free Induction Decay and Spin Diffusion" (1968) *Phys. Rev.* 167, 282–288.
- C.Tang, J. S. Waugh "Dynamics of classical spins on a lattice: Spin diffusion" (1992) *Phys. Rev. B* 45, 748–754
- D. Greenbaum, M. Kindermann, C. Ramanathan, D. G. Cory "Hydrodynamic approach to coherent nuclear-spin transport" (2005) *Phys. Rev. B.* 71, 054403

# Ratio of the diffusion coefficients and relaxation times reflect local anisotropy

$$\frac{D_z[001]}{D_z[111]} = 1.4 \pm 0.2$$

$$\frac{T_1[111]}{T_1[001]} = 1.1 \pm 0.1$$

- Angular variation due to anisotropy in the dipolar coupling; dipolar coupling stronger along the [001] direction than [111] direction

$$b_{ij} = \frac{1}{4} \gamma^2 \hbar^2 \frac{(1 - 3 \cos^2 \theta_{ij})}{r_{ij}^3}$$



# Dipolar order: Comparison with theory & simulation

Theoretical studies of $D_E$	$D_E[001]$ $\times 10^{-12}$ [cm <sup>2</sup> /s]	$D_E[111]$ $\times 10^{-12}$ [cm <sup>2</sup> /s]	$\frac{D_E[001]}{D_E[111]}$	$\frac{D_E[001]}{D_Z[001]}$	$\frac{D_E[111]}{D_Z[111]}$
Irreversible Statistical Mechanics (Borckmans and Walgraef)	8.53	7.43	1.16	1.22	1.49
Simulation of classical gyro-magnets (Tang and Waugh)	13.3	No data	-	1.79	-
Hydrodynamic Approach (D. Greenbaum et. al.)	19.1	11.4	1.7	2.35	1.54

## Experimental results

$$\frac{D_E[001]}{D_Z[001]} = 4.5 \pm 0.8 \quad \frac{D_E[111]}{D_Z[111]} = 7.5 \pm 1.2 \quad \frac{D_E[001]}{D_E[111]} = 0.9 \pm 0.1$$

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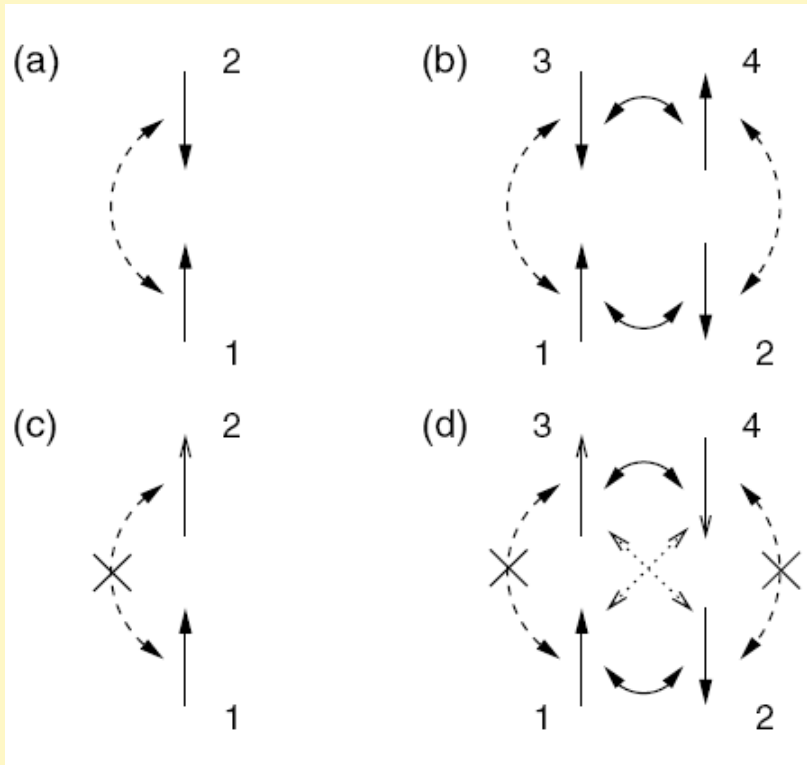
# Experimental results

$$\begin{array}{c} \frac{D_E [001]}{D_Z [001]} = 4.5 \pm 0.8 \\ \\ \frac{T_1 [001]}{T_{1D} [001]} = 28 \pm 0.5 \end{array} \left| \begin{array}{c} \frac{D_E [111]}{D_Z [111]} = 7.5 \pm 1.2 \\ \\ \frac{T_1 [111]}{T_{1D} [111]} = 30 \pm 1.0 \end{array} \right| \begin{array}{c} \frac{D_E [001]}{D_E [111]} = 0.9 \pm 0.1 \\ \\ \frac{T_{1D} [001]}{T_{1D} [111]} = 0.9 \pm 0.1 \end{array}$$

- Spin diffusion rate of dipolar order is isotropic with respect to crystal orientation.
- Differences in the spin diffusion rate of dipolar order to Zeeman order do not account for differences in corresponding relaxation times (perhaps other processes are involved?).

# Simple schematic highlights why diffusion of dipolar order is less quenched

For diffusion of Zeeman order both spins 1 and 2 must undergo a flip flop



If spins 1 and 2 are initially in the same state (both  $\uparrow$  or both  $\downarrow$ ), no evolution takes place

For the diffusion of dipolar order along the  $z$  direction, there are the two possibilities: both spins 1 and 3, and spins 2 and 4, can flip, or spins 1 and 2, and spins 3 and 4, can flip

Even if states 3 and 4 are initially  $\uparrow$  and  $\downarrow$ , two different evolution paths are present. Spins 1 and 2 can flip and spins 3 and 4 can flip or spins 1 and 4 and spins 2 and 3 can flip.

# Conclusions

- The spin diffusion rate of a two spin correlated spin state in single crystal calcium fluoride was measured using pulsed gradient schemes.
- Coherent averaging techniques were applied to correct for a variety of pulse errors in the ‘magic-echo’ cycle resulting in more accurate control over the nuclear spin degrees of freedom. These methods are also applicable for investigations relating to spectroscopy and imaging.
- The experimental methodology allows for further tests of many-body physics ex: studies of spin diffusion as a function of polarization or dimensionality.

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