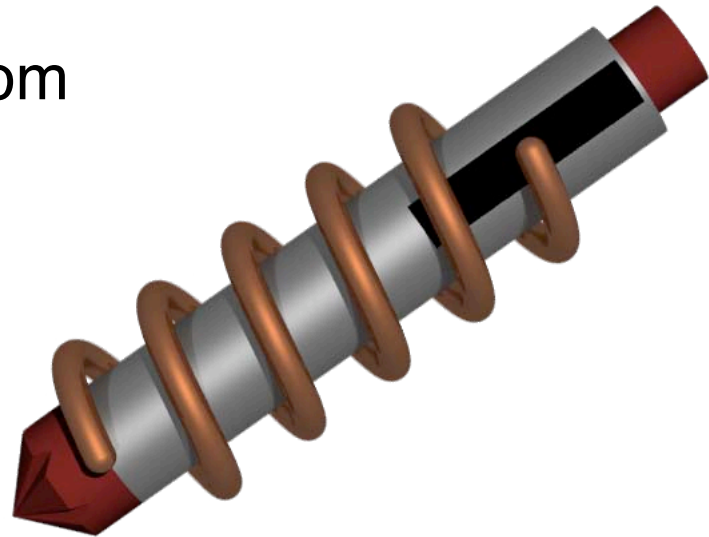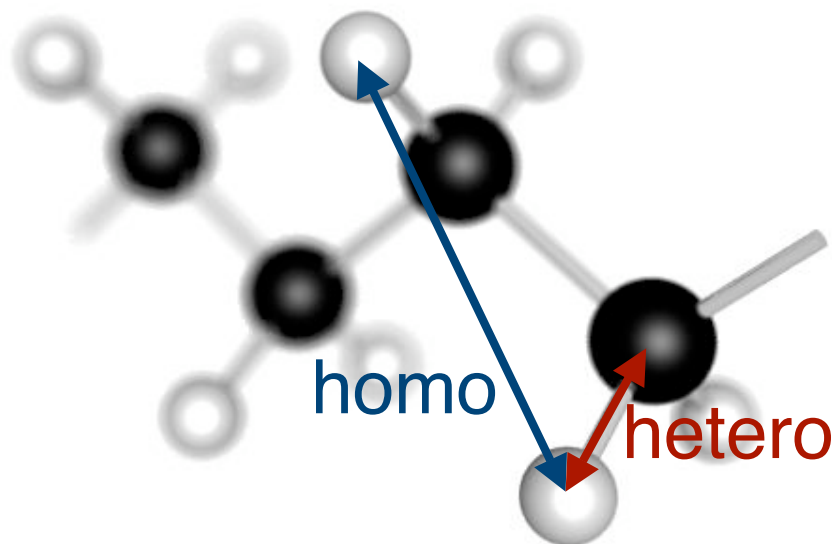# Solids

- Why spectra for solids are broad
- How to make them narrow and informative
- How to get useful info from anisotropic interactions
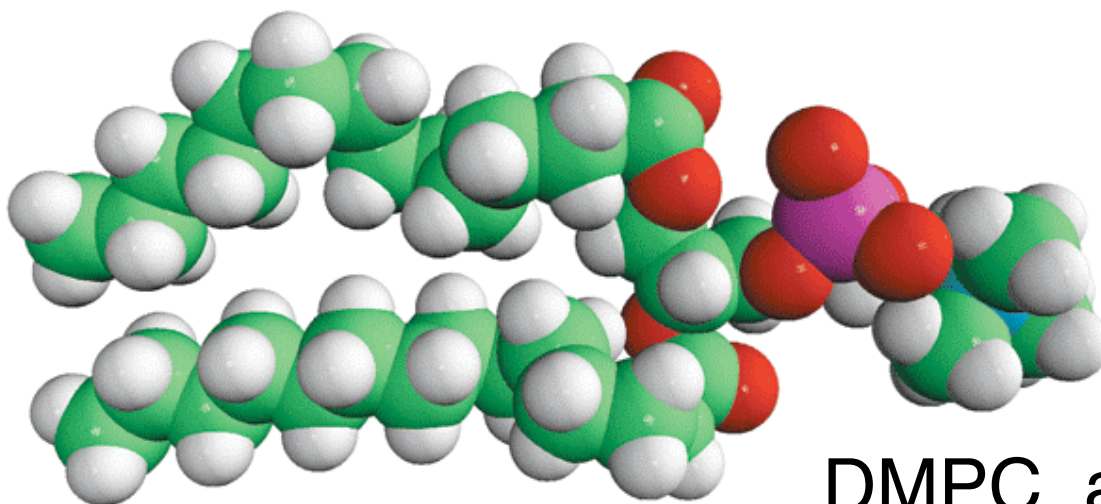
Homo- and heteronuclear couplings

- Homonuclear: same kind of nuclei
  - Ex. ^1H-^1H
- Heteronuclear: different kinds of nuclei
  - Ex. ^1H-^{13}C, ^1H-^{15}N
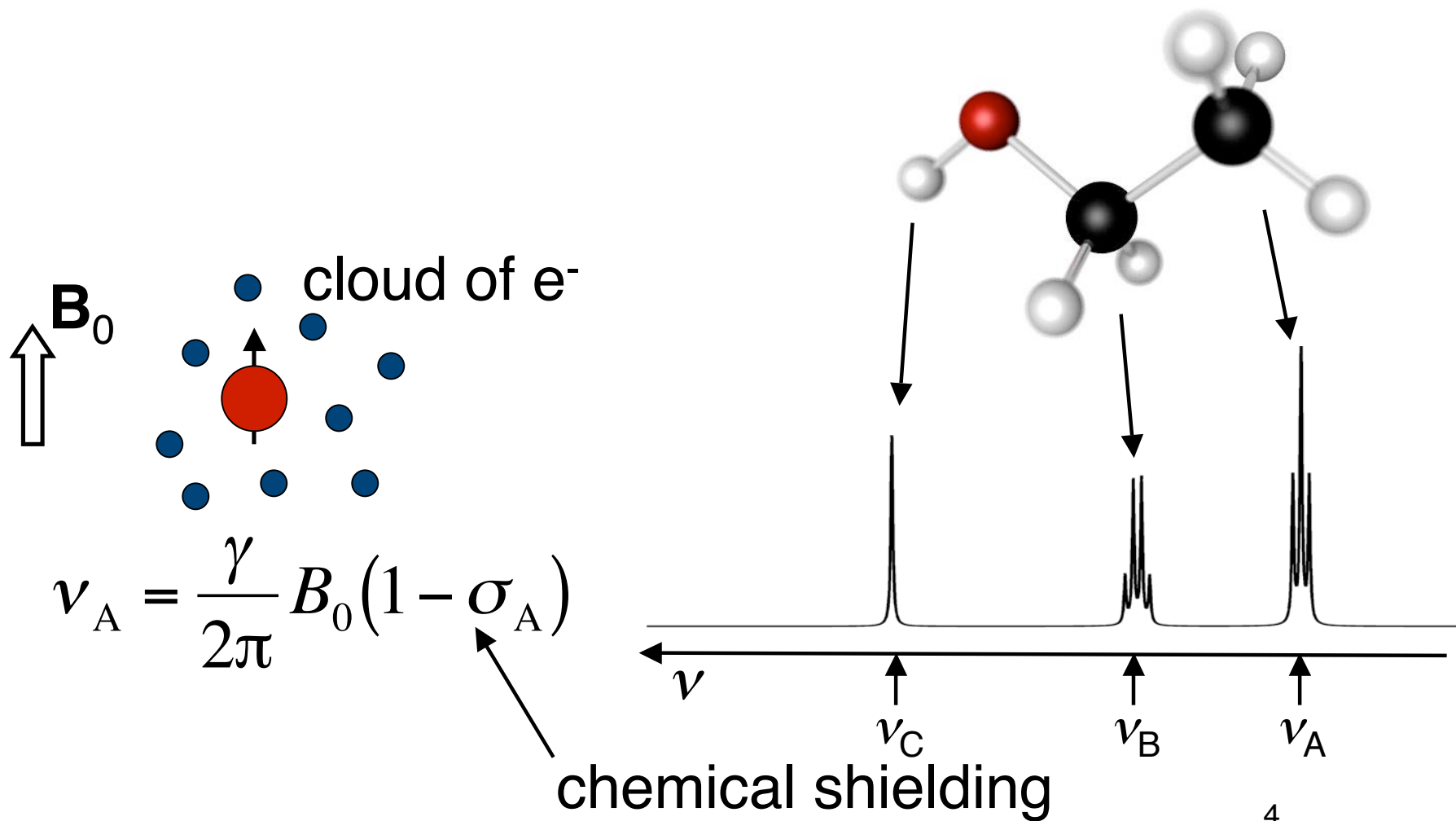
Abundant and dilute spins

- Abundant, ^{1}H

- Isotopically dilute, ^{13}C, ^{2}H ⎫ homonuclear
- Chemically dilute, ^{31}P ⎬ interactions can be
  ⎭ neglected

Fig from Avanti website

DMPC, a phospholipid

Chemical shift

$$\nu_A = \frac{\gamma}{2\pi} B_0 \left(1 - \sigma_A\right)$$

cloud of e⁻

$\mathbf{B}_0$

chemical shielding

ν

ν_C ν_B ν_A

4

Solids vs. liquids

cellulose + H_2O

liquid

solid

-50   0   50

^1H shift / kHz

surfactant in D_2O

5   4   3   2   1   0

^1H shift / ppm
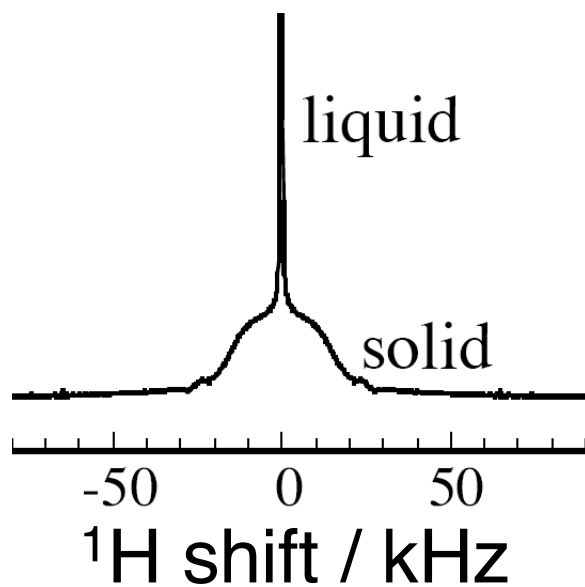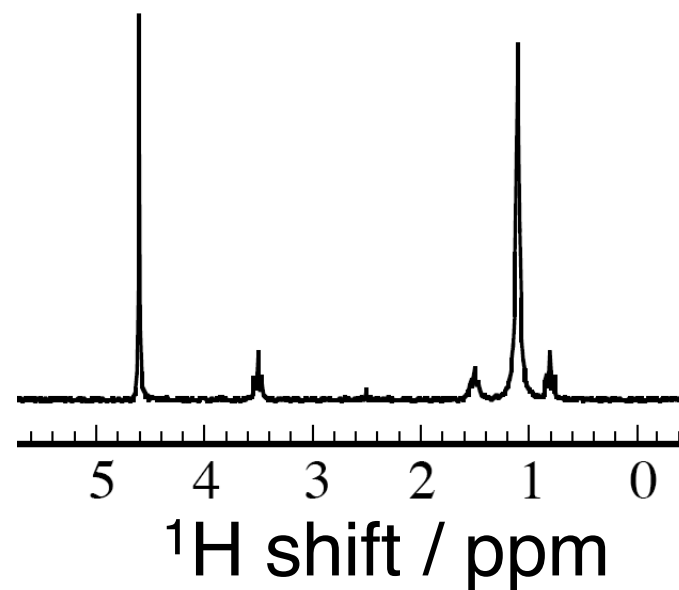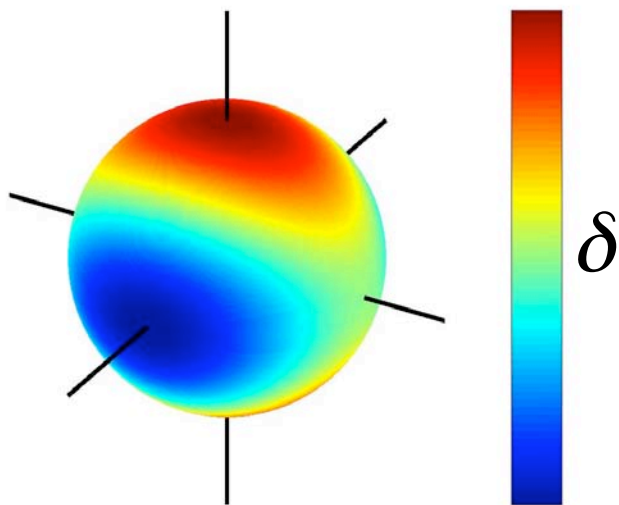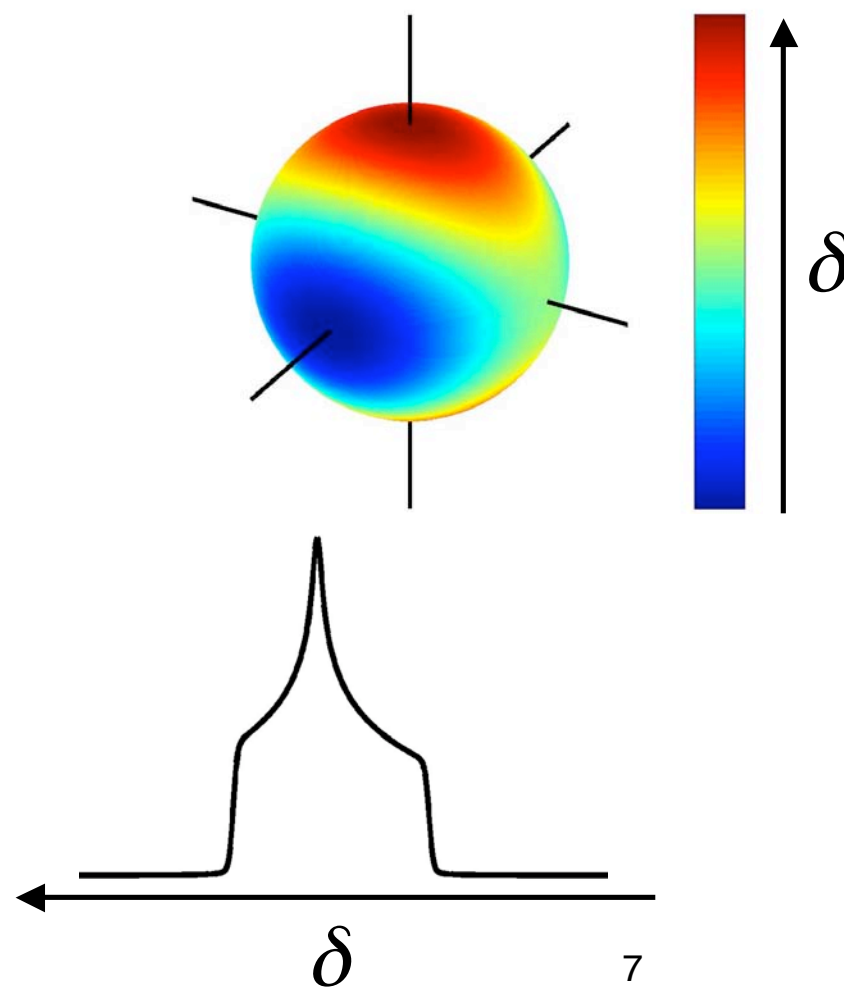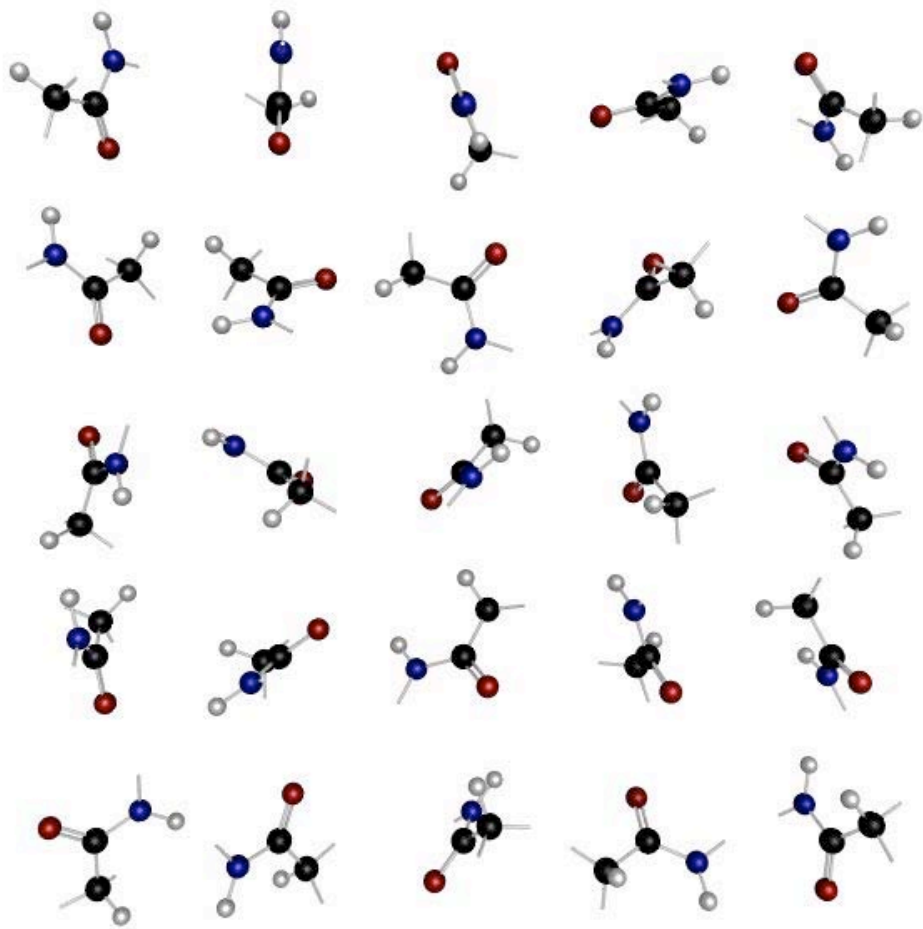
Chemical shift anisotropy (CSA)

- Shift depends on relative orientation B_0 - molecular frame
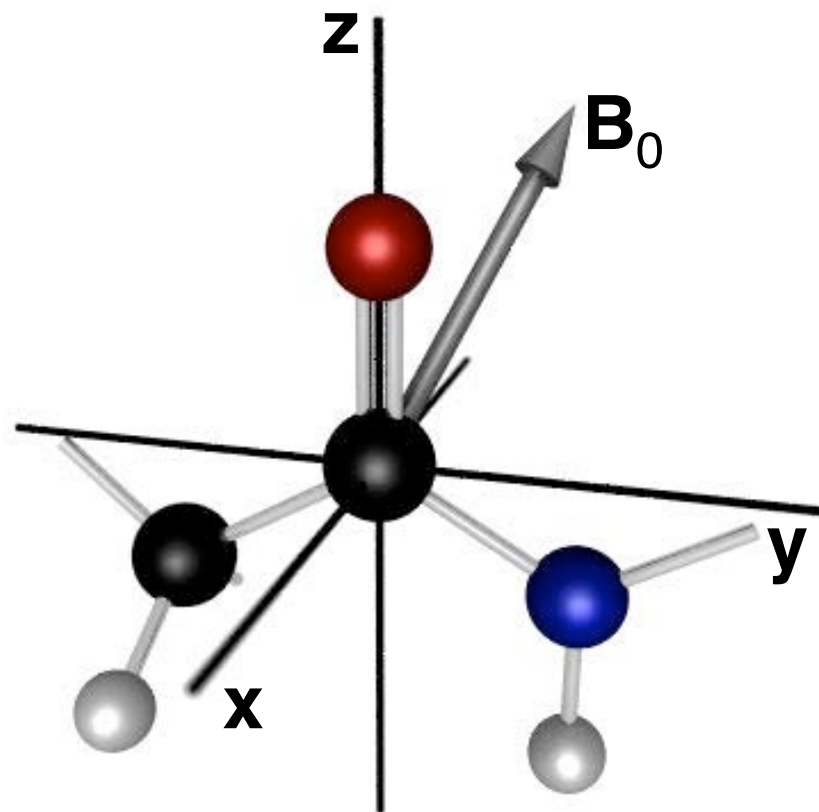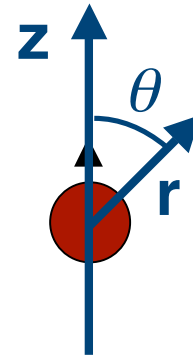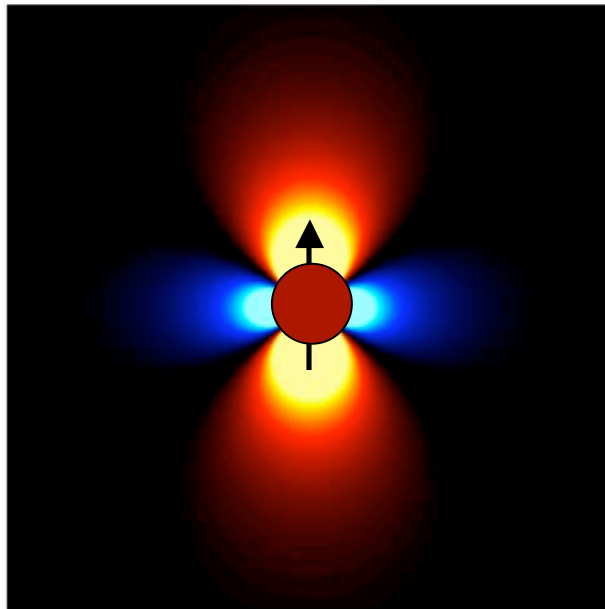
Powder patterns

Field from a magnetic dipole
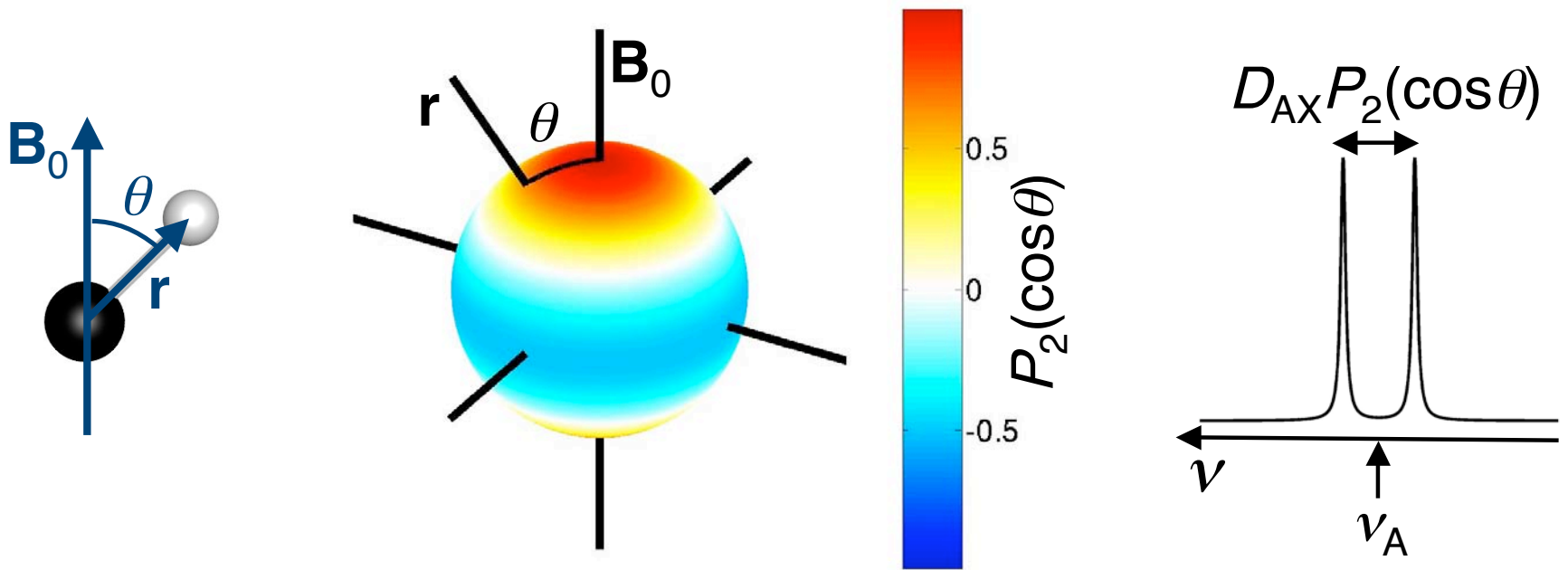
$$B_z \propto \frac{P_2(\cos\theta)}{r^3}$$

$$P_2(\cos\theta) = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$
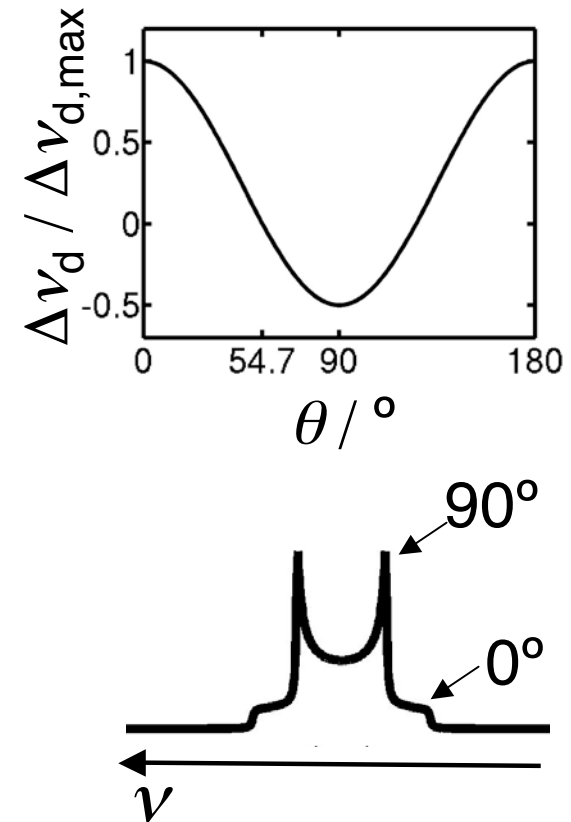
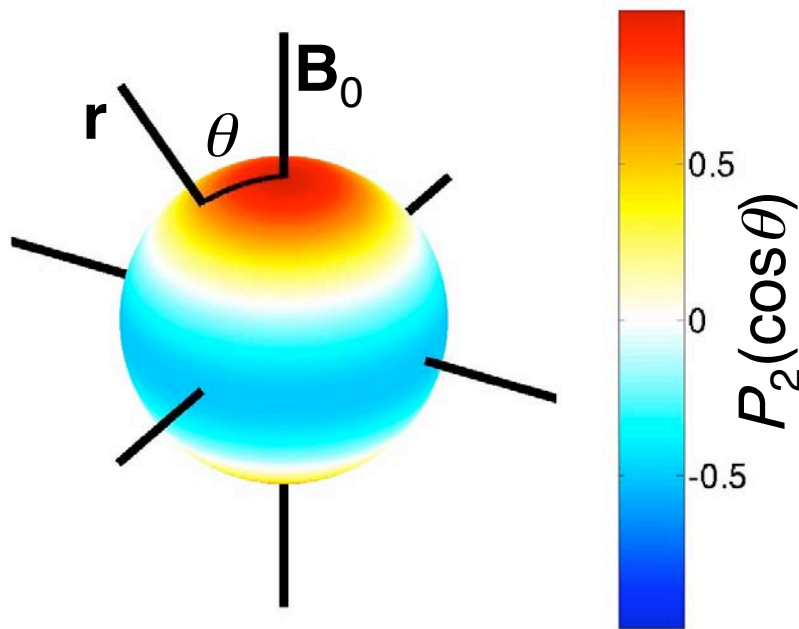2nd Legendre polynomial, P_2

Dipolar coupling - anisotropic

$$\upsilon_A = \frac{\gamma}{2\pi} B_0 (1 - \sigma_A) \pm \frac{1}{2} D_{AX} P_2 (\cos\theta)$$
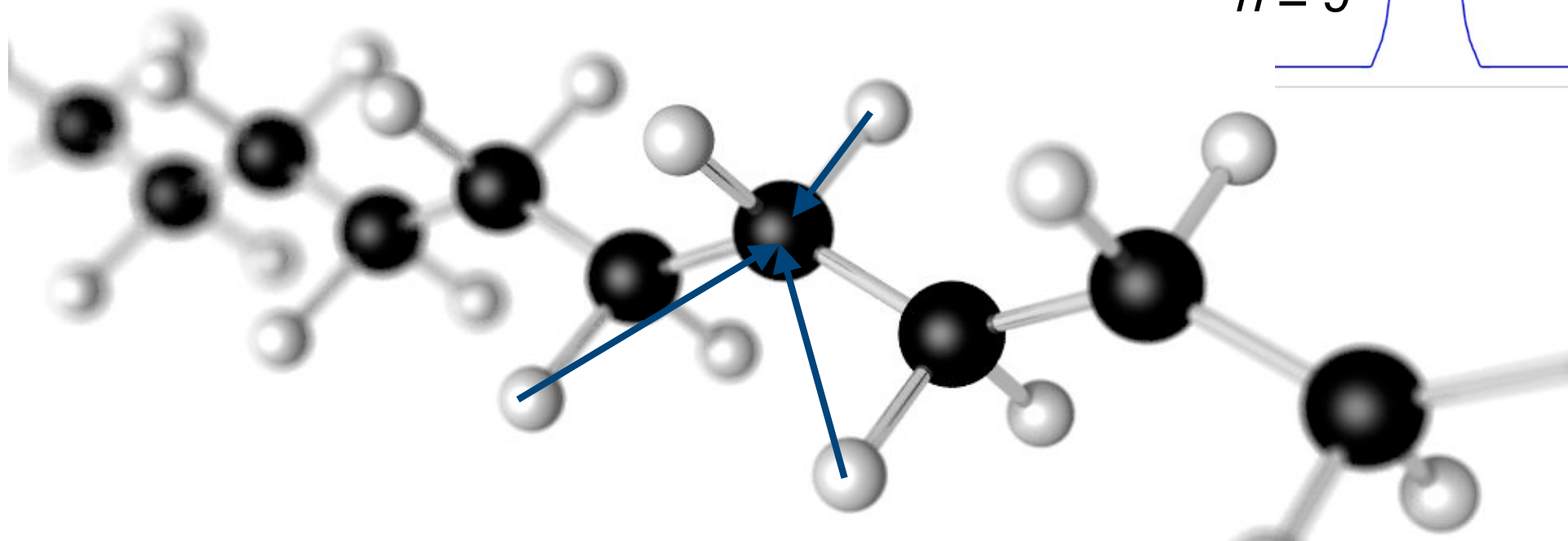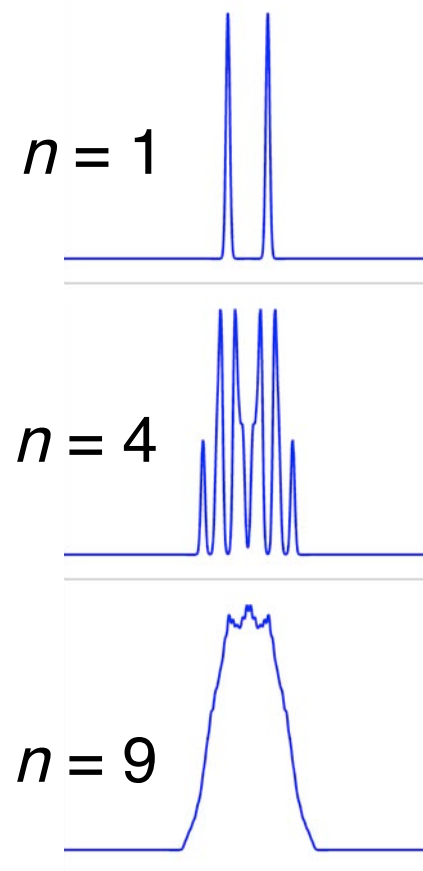

2nd Legendre polynomial, P_2

Pake pattern

B_0

r

θ

$P_2(\cos\theta)$

$\Delta\nu_d / \Delta\nu_{d,max}$

$\theta /\,^{\circ}$

90°

0°

ν

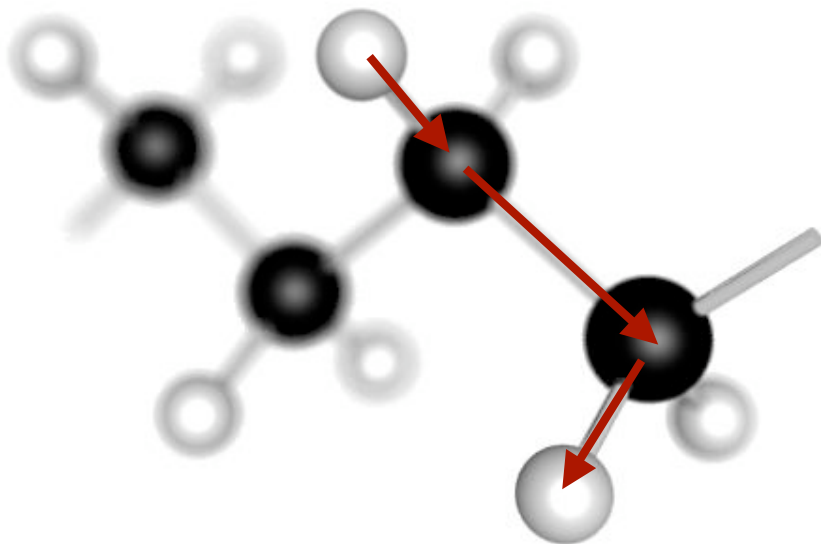- One orientation: doublet
- Random orientations: Pake pattern

Multiple couplings

- Number of lines = 2^n
- Width: "strength" of couplings

$n = 1$

$n = 4$

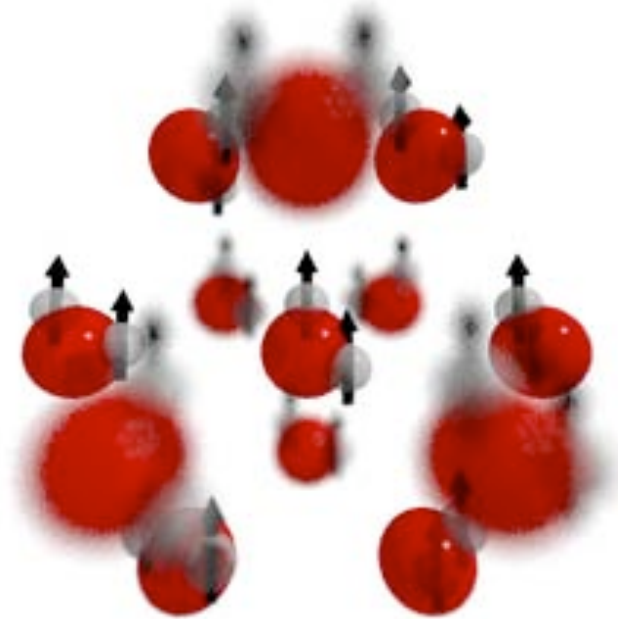$n = 9$

Scalar coupling - isotropic

$$\upsilon_{\mathrm{A}} = \frac{\gamma}{2\pi} B_0 \left(1 - \sigma_{\mathrm{A}}\right) \pm \frac{1}{2} J_{\mathrm{AX}}$$
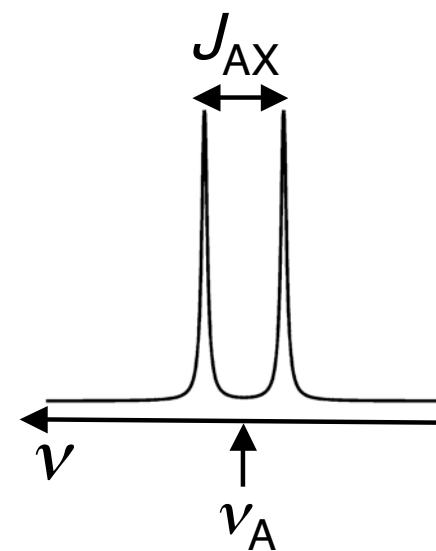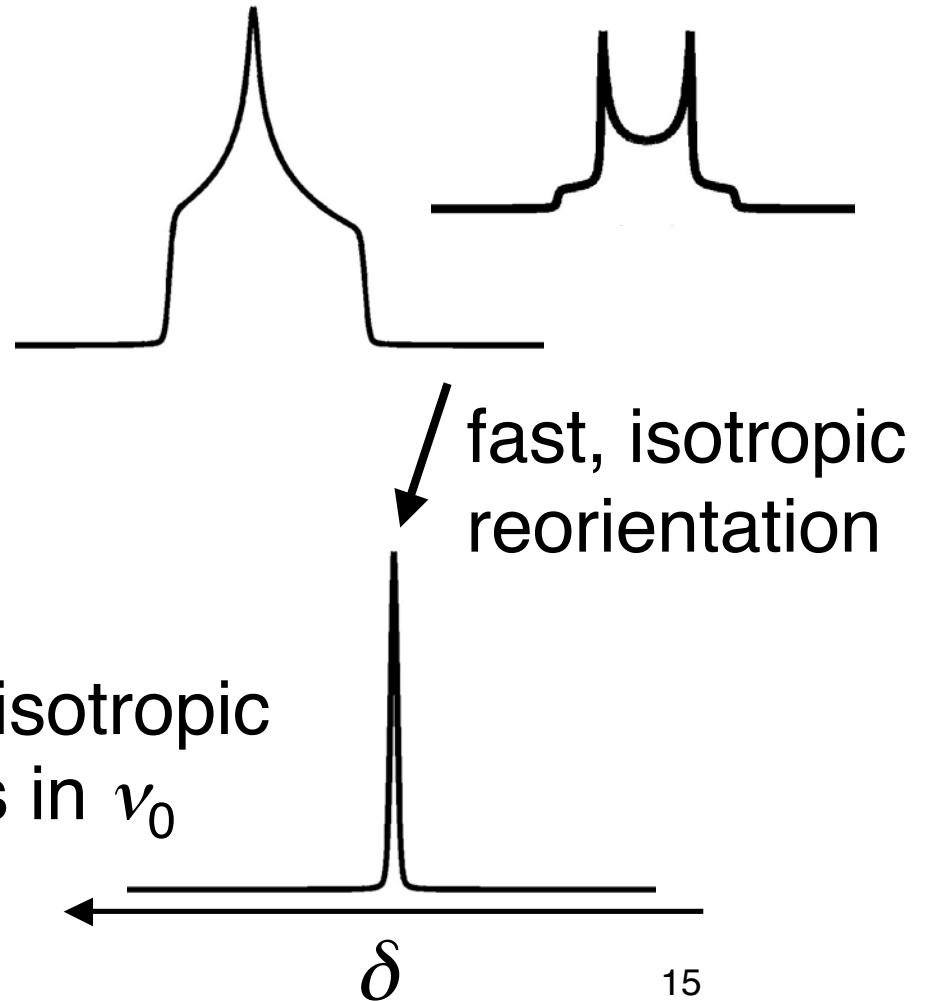
Origin of linewidth in solids

- Anisotropic interactions
  - Chemical shift anisotropy
  - Dipolar couplings
  - (Quadrupolar couplings, …)
- How to get the isotropic chemical shift?
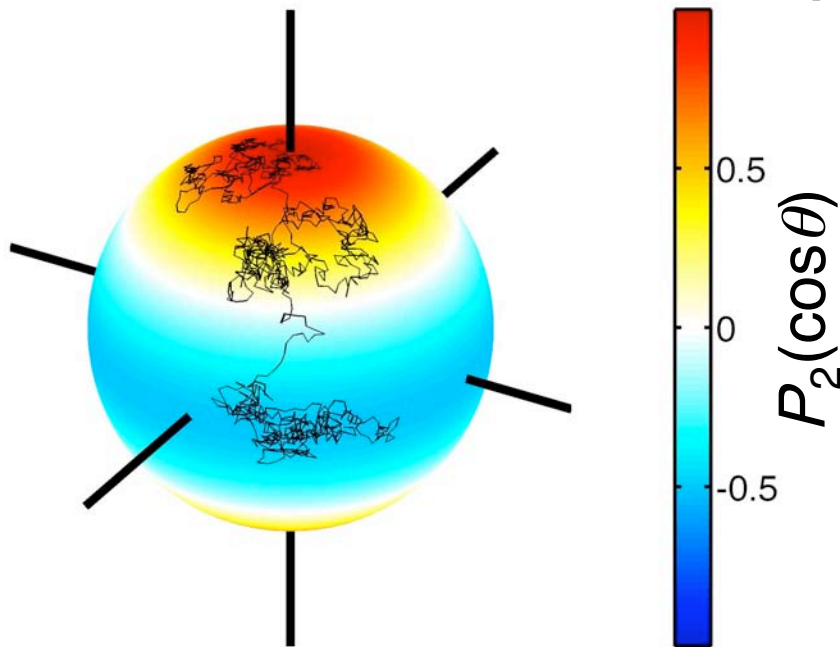
Molecular motion in liquids

Averaging by motion

fast, isotropic reorientation

- Single peak if rate of isotropic motion >> differences in ν_0

δ

15

Rotational motion in liquids

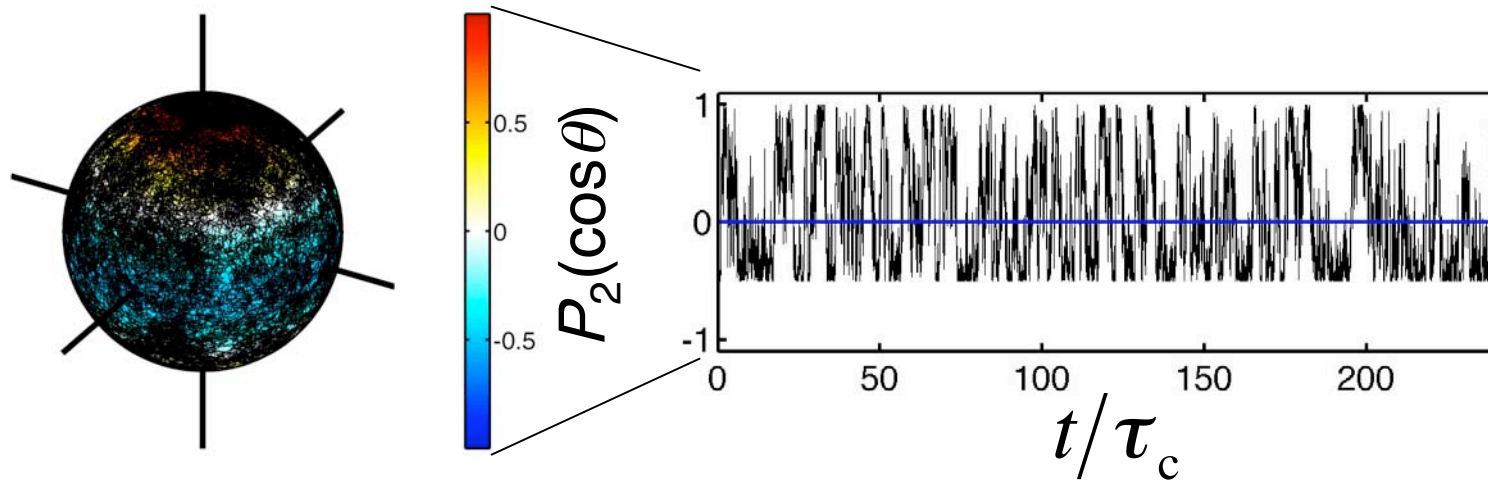- Tumbling
- Random walk on a sphere

$P_2(\cos\theta)$

dipole pair

Fluctuating dipolar field, B_z
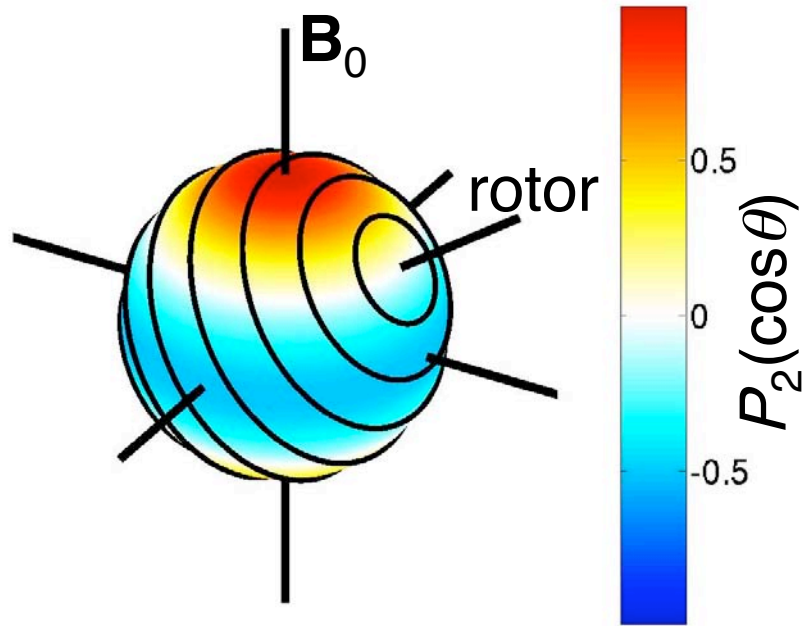

$P_2(\cos\theta)$

t/τ_c

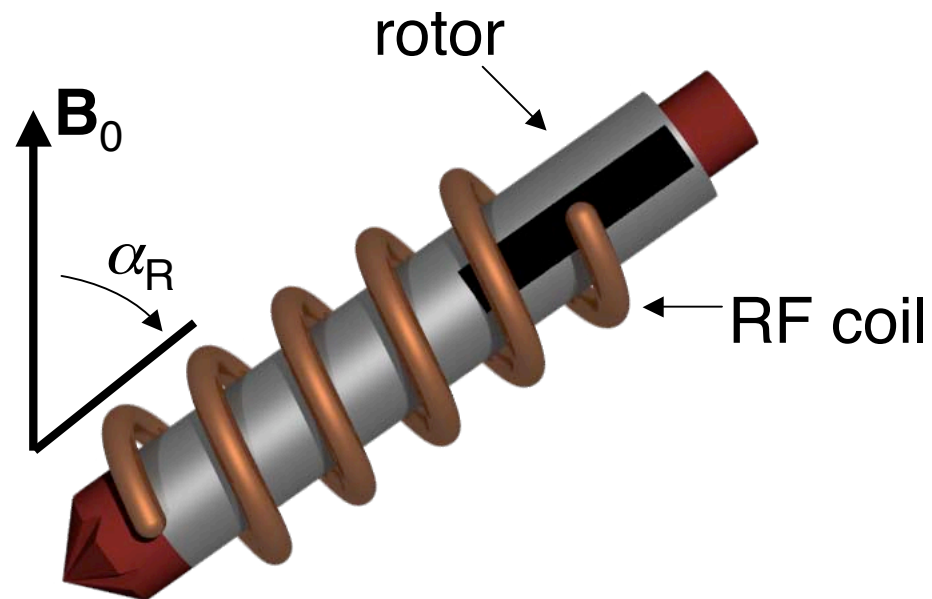correlation time
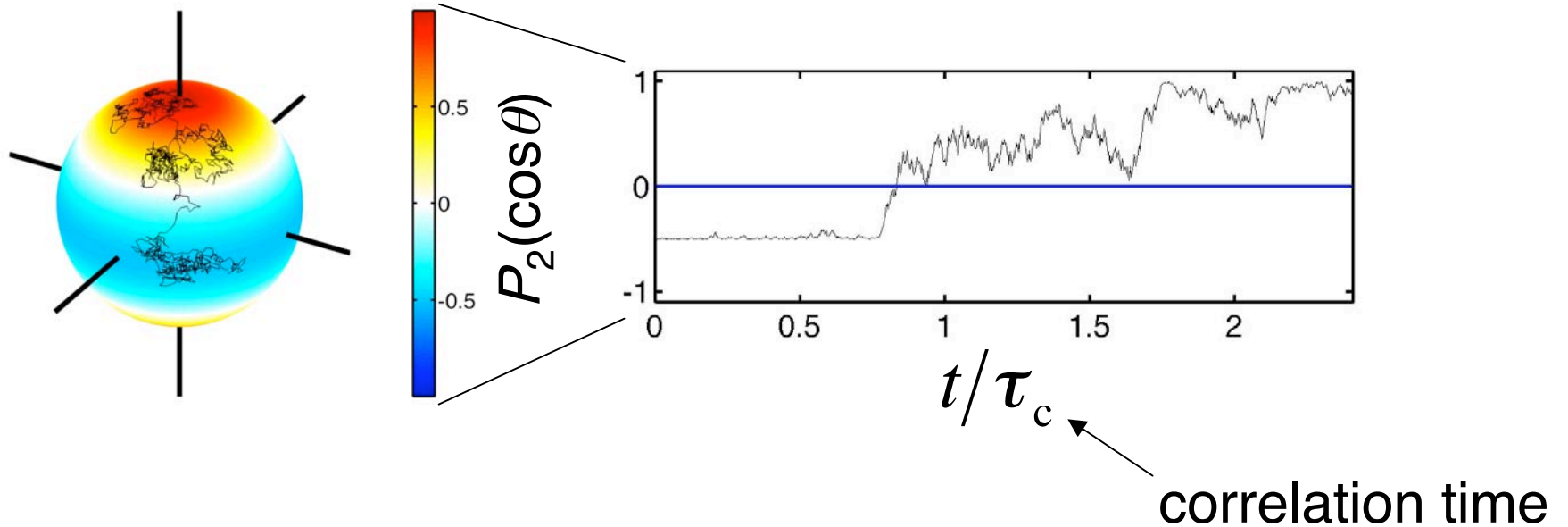
Fluctuating dipolar field, B_z

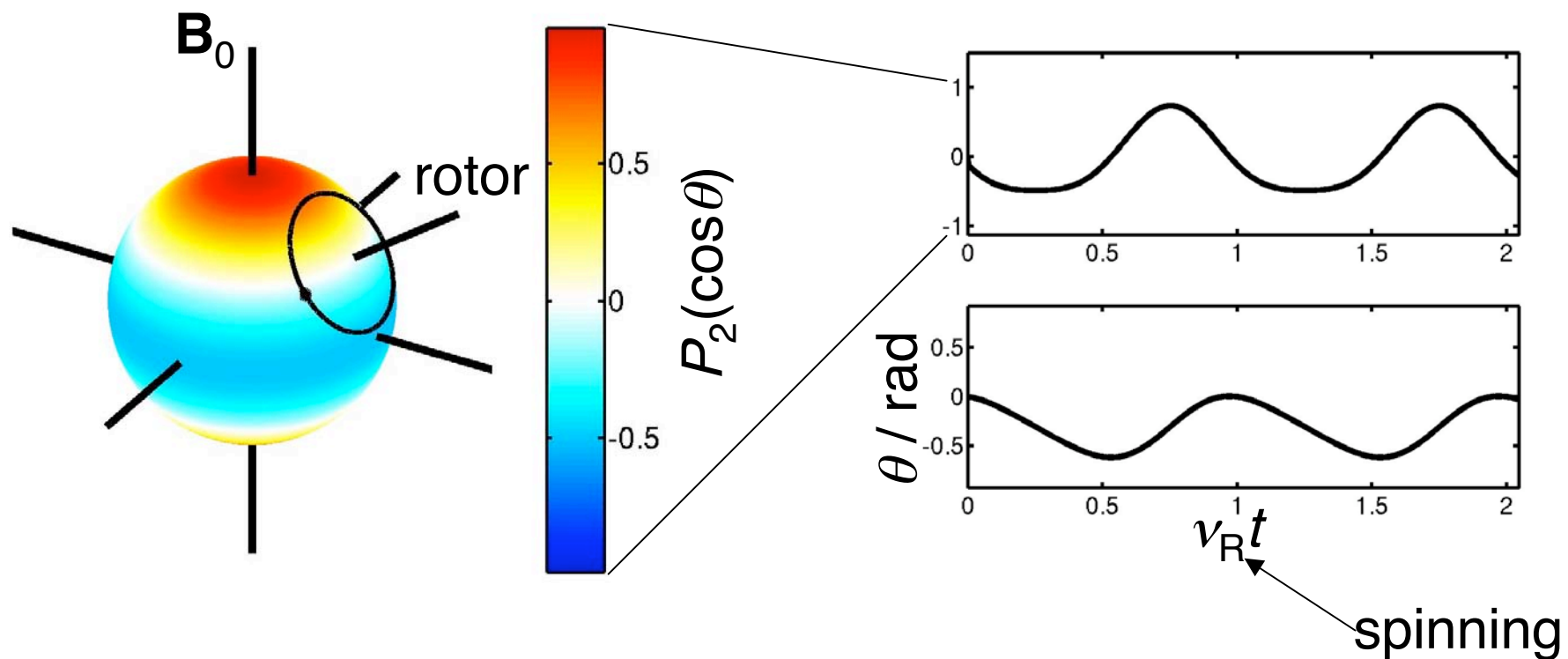Average interaction = 0! (if isotropic)

Dipolar coupling during rotation

Sample spinning

Rotation at rate ν_r (~10 kHz)

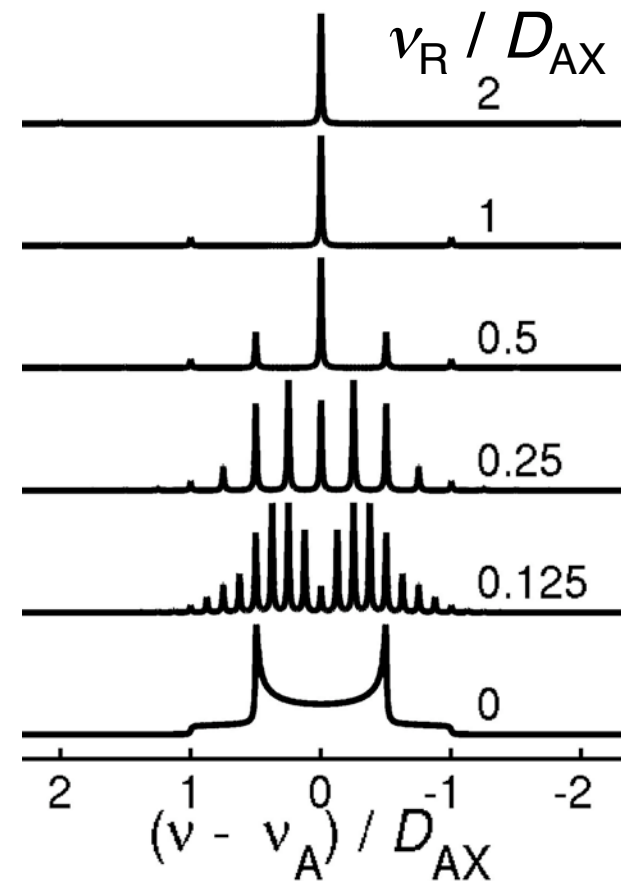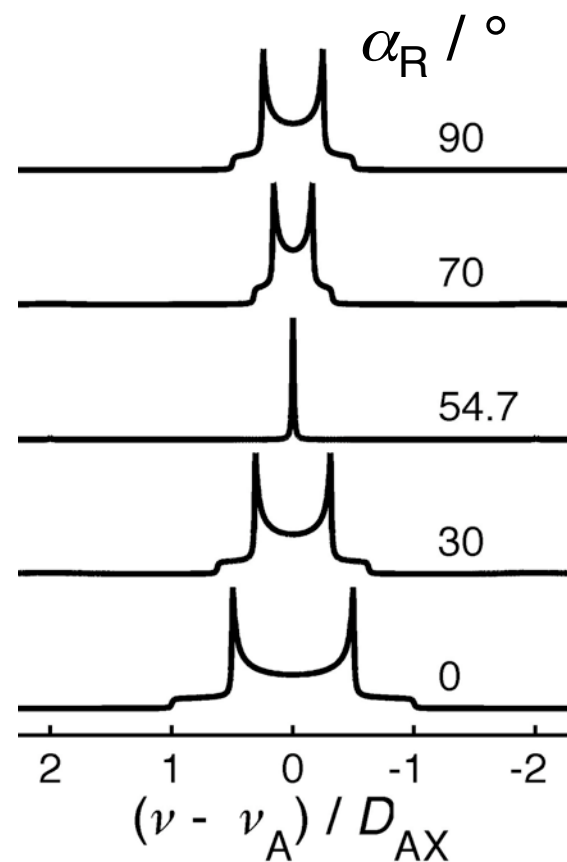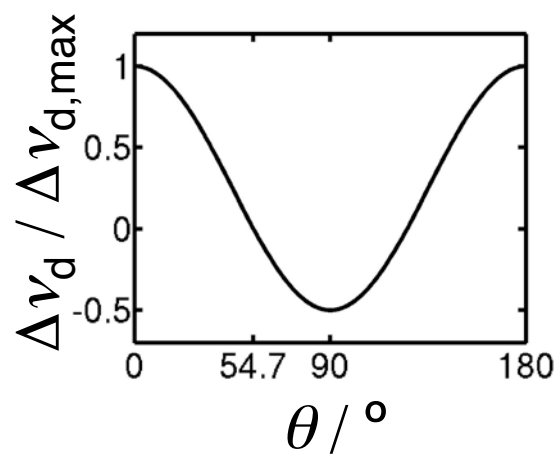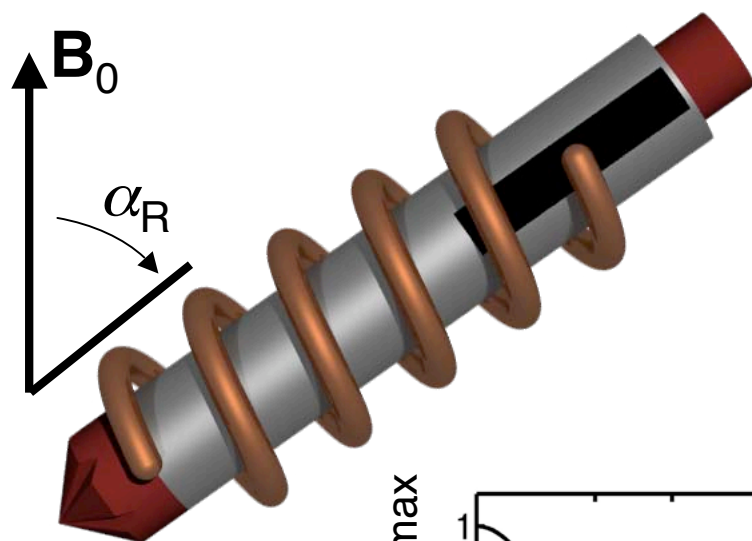# Magic angle = 54.7°

Average interaction = 0 if $\alpha_R = 54.7°$

Effect of spinning rate, ν_R

- Isotropic spectrum of A if $\nu_R \gg D_{AX}$, CSA

- Spinning sidebands at multiples of ν_R

ν_R / D_{AX}

2

1

0.5

0.25

0.125

0

$2 \quad 1 \quad 0 \quad -1 \quad -2$

$(\nu - \nu_A) / D_{AX}$

Effect of spinning angle, α_R

B_0

α_R

α_R / °

90

70

54.7

30

0

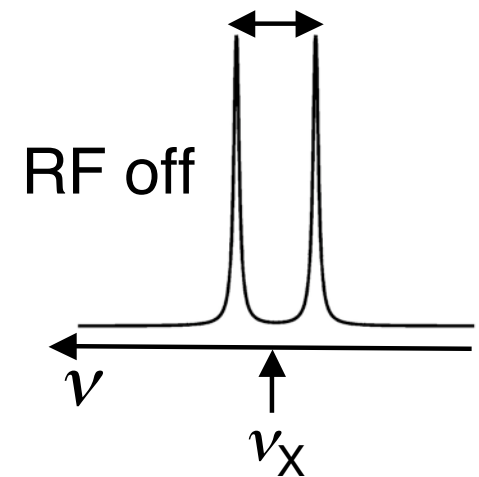$\Delta\nu_d / \Delta\nu_{d,max}$

θ / °

$(\nu - \nu_A) / D_{AX}$

23

RF decoupling

- B_1 field at A resonance

    $v_{1,dec} = -\gamma B_{1,dec}$ (50 kHz)

- No splitting of X if $v_{1,A} >> J_{AX}, D_{AX}$
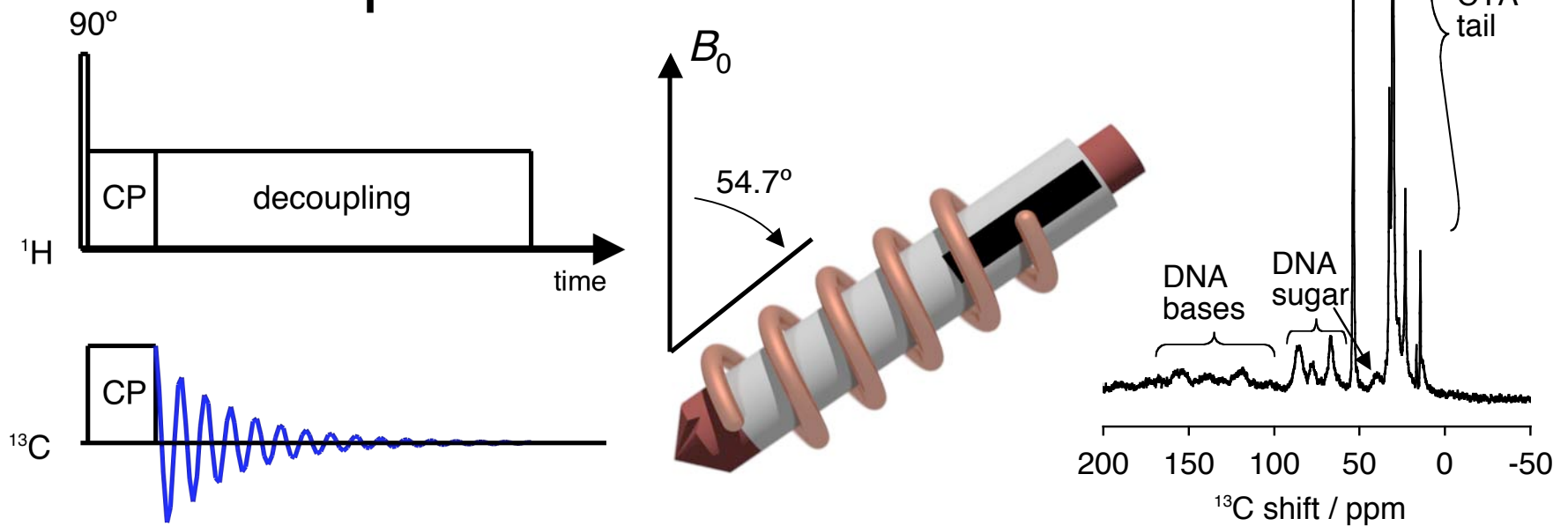
RF on

RF off

v

v_X
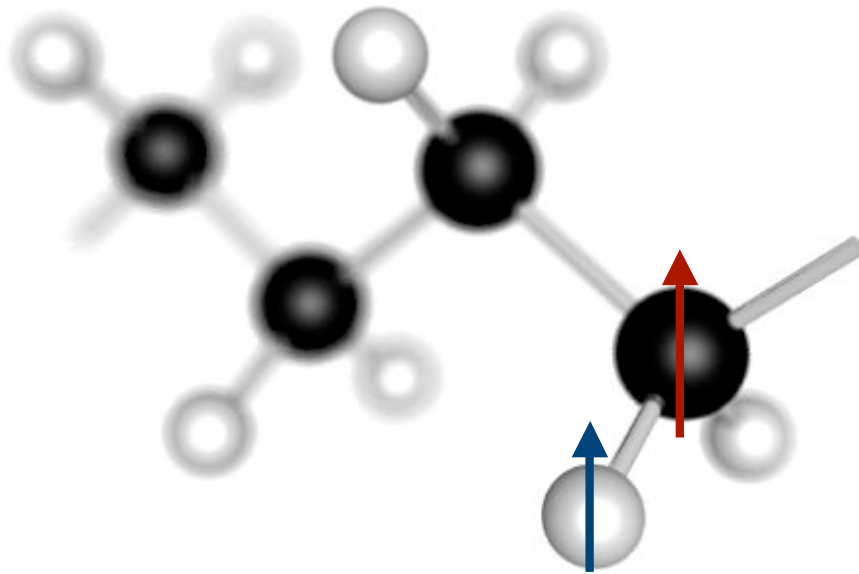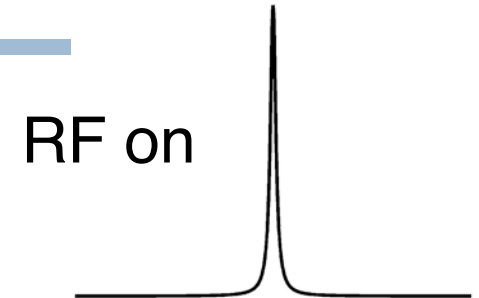
Cross-polarization (CP)

- Transfer of magnetization from ^{1}H to X nucleus (^{13}C, ^{31}P, ^{15}N, etc.)

- Simultaneous B_1 fields with strength $\nu_{1,H}$ and $\nu_{1,X}$ at ^{1}H and X frequencies

- Resonance if $\nu_{1,H} = \nu_{1,X}$

  Hartmann-Hahn condition
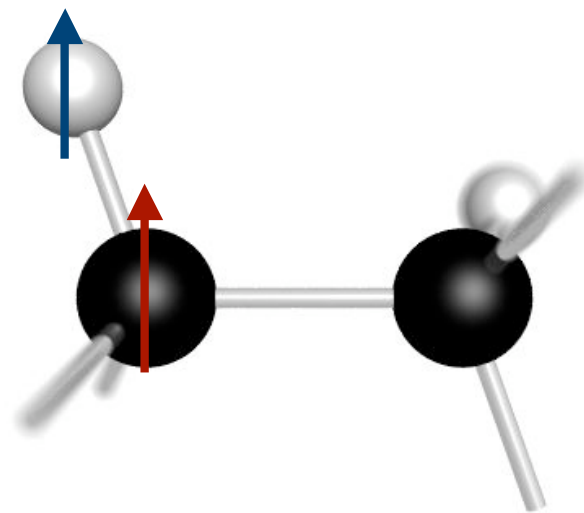
CP/MAS NMR

- High-power ^1H decoupling
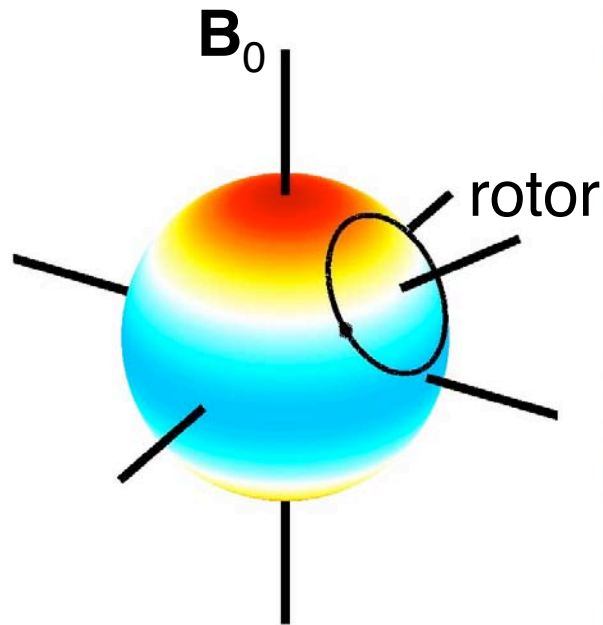- Magic-angle spinning
- Cross polarization

One strength of NMR: Switching interactions on/off

- Interaction
  - chemical shift
  - chemical shift anisotropy
  - dipolar couplings (homo, hetero)
  - J-couplings (homo, hetero)
  - B_0 inhomogeneity
  - …

- Tool
  - MAS
  - decoupling
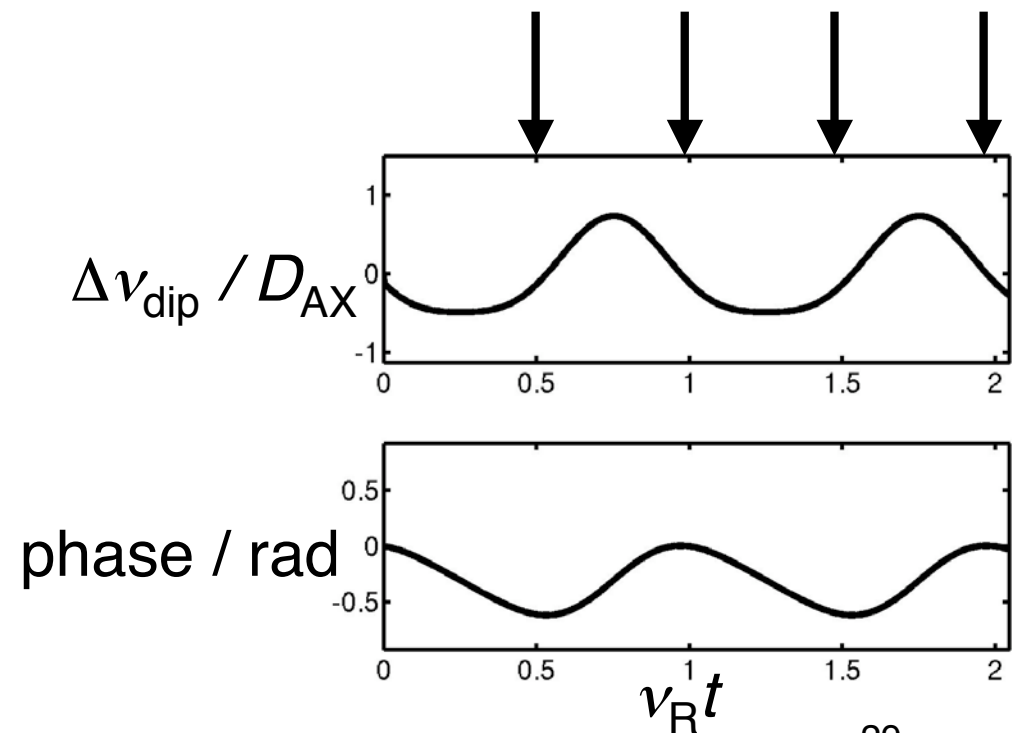 - spin echo
  - B_0 strength
  - gradients
  - …

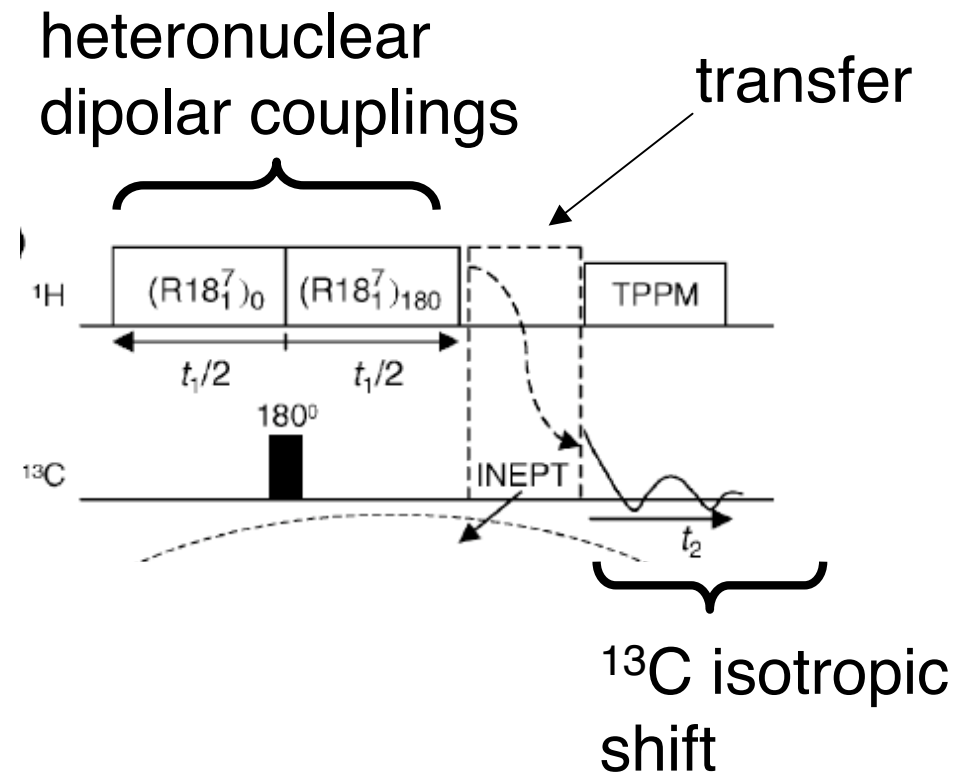# Heteronuclear shift correlation HETCOR
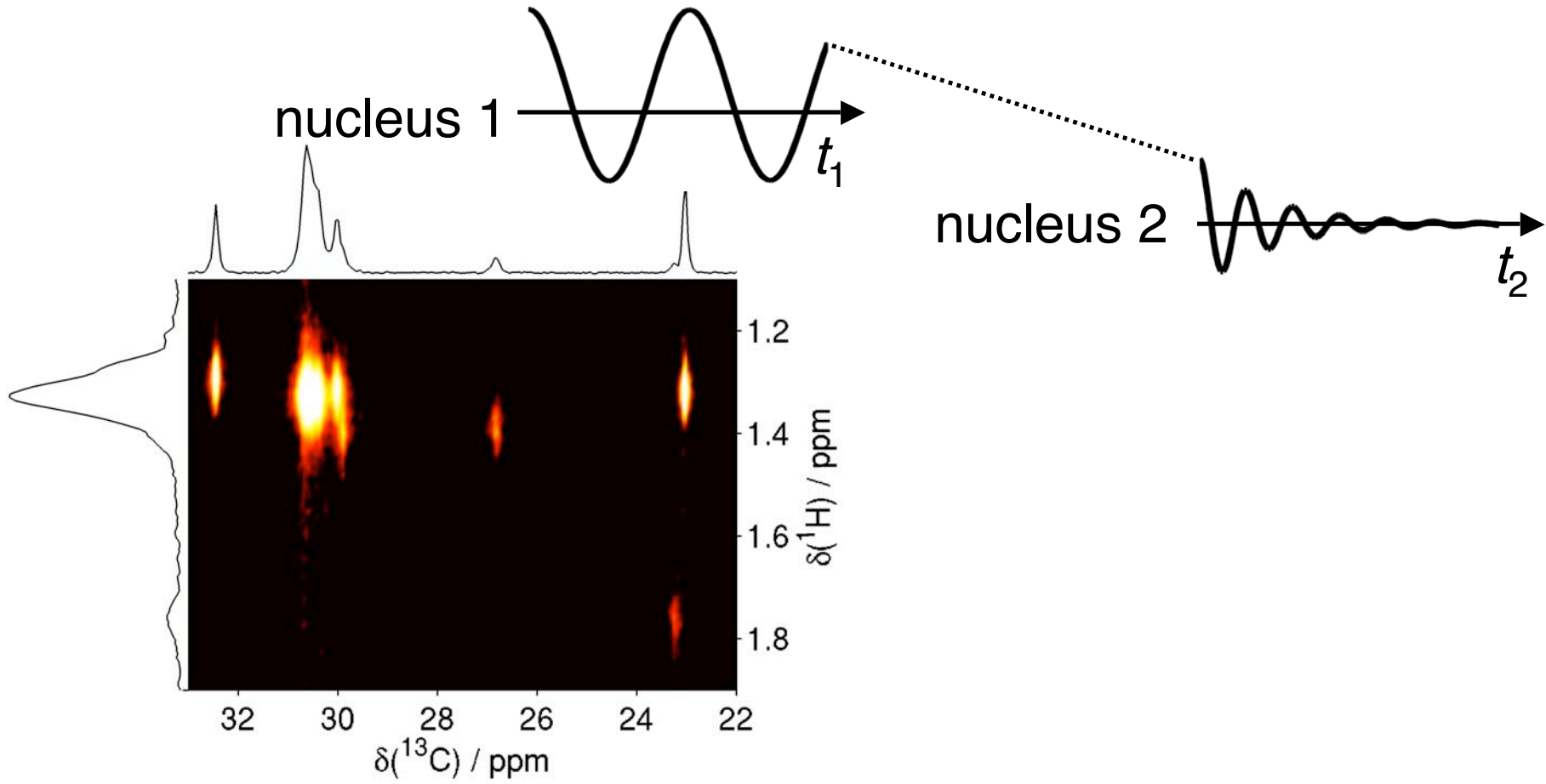
Decoupling and recoupling

MAS averaging would be spoiled by rotor-synchronized 180° pulses

$\mathbf{B}_0$

rotor

$\Delta\nu_{\text{dip}} / D_{\text{AX}}$

phase / rad

$\nu_R t$

Separated local field

Separated local field