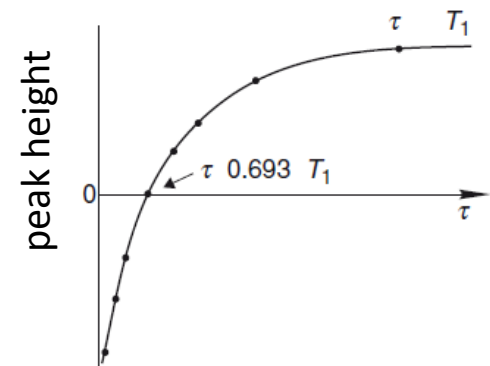
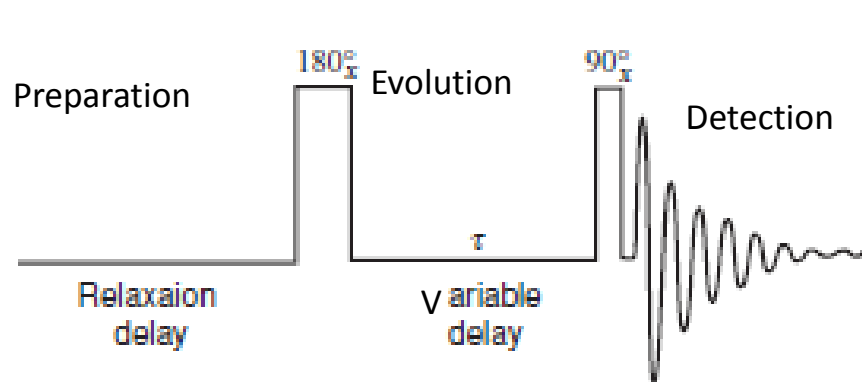
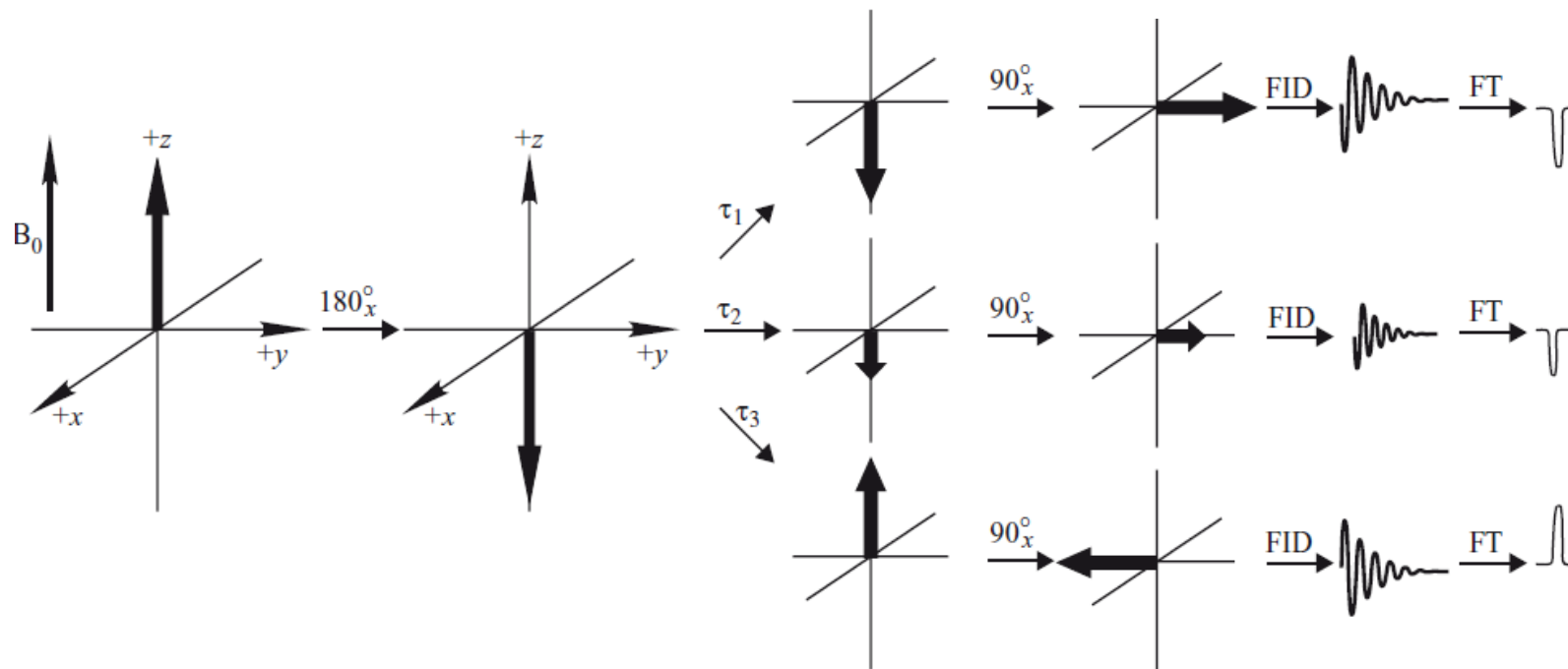


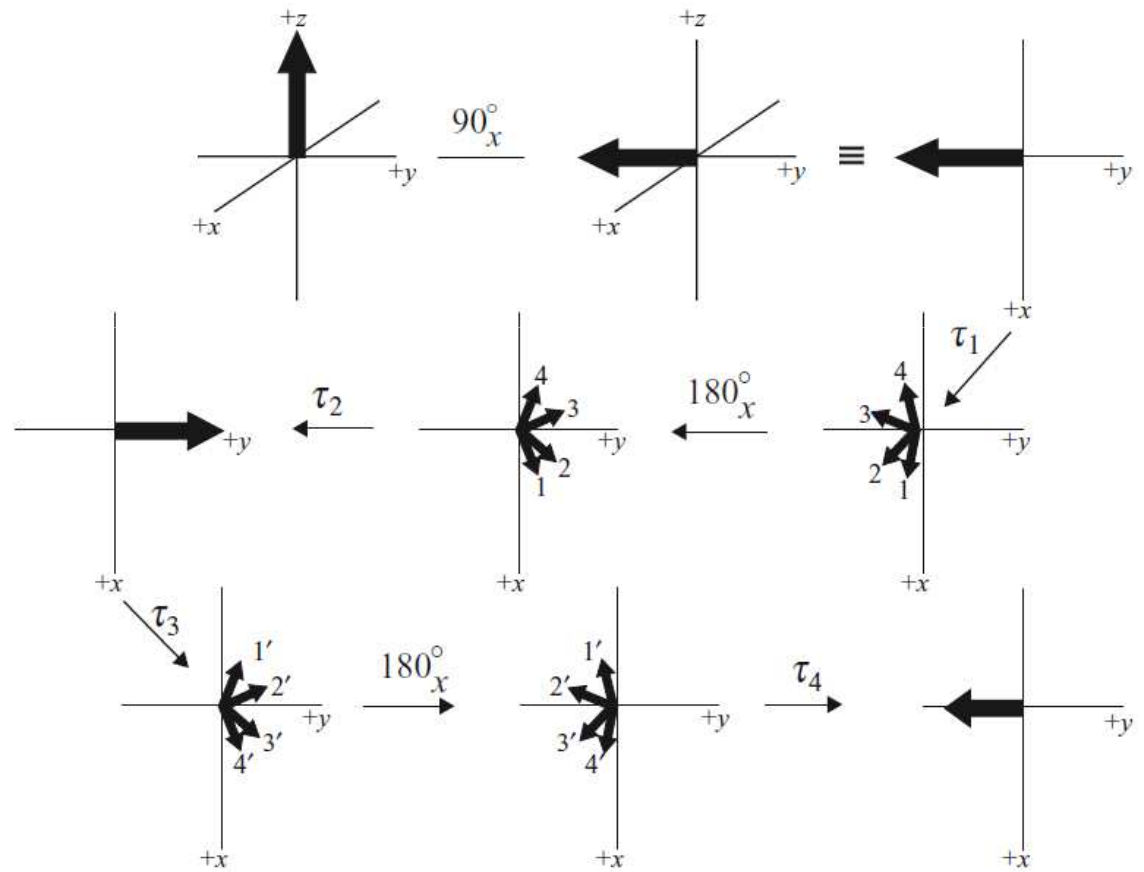
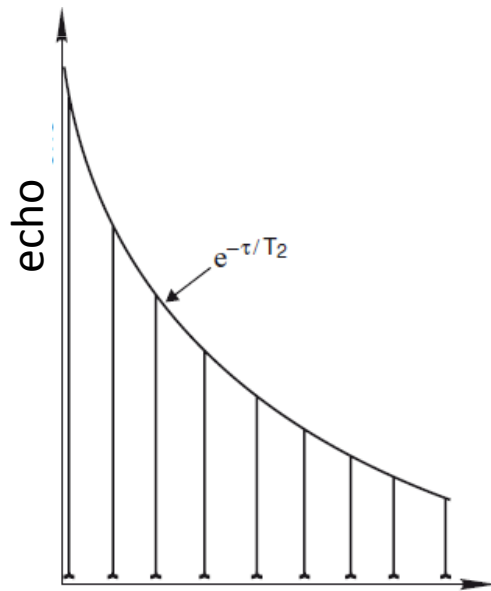
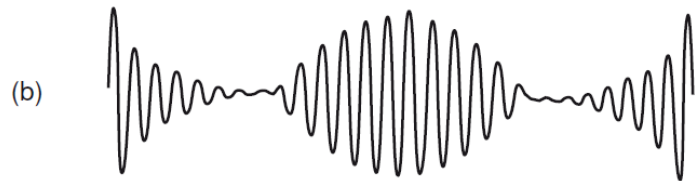
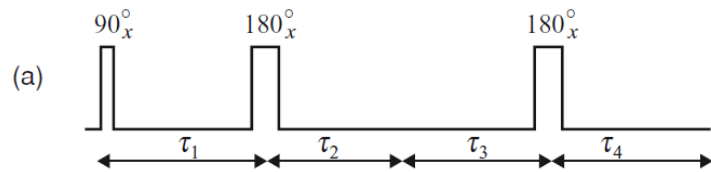
Multiple-pulse experiments: Inversion recovery method



$$I = I_{\infty}[1 - 2\exp(-\tau/T_1)] \quad (43)$$

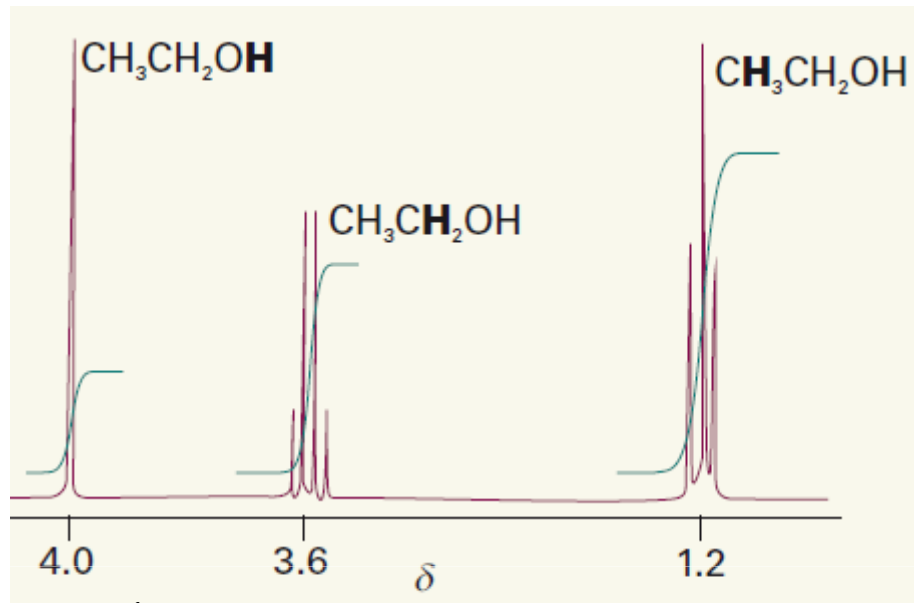


The spin-echo effect to measure T_2

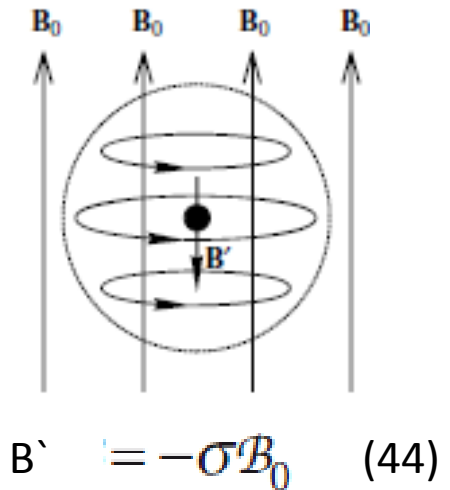


The amplitude is reduced by T_2 relaxation

The chemical shift



The ^1H -NMR spectrum of ethanol.



total local field:

$$\mathcal{B}_{\text{loc}} = \mathcal{B}_0 + \delta \mathcal{B} = (1 - \sigma) \mathcal{B}_0 \quad (45)$$

$$\sigma_{\text{iso}} = \frac{1}{3}[\sigma_{11} + \sigma_{22} + \sigma_{33}] = \frac{1}{3}[\sigma_{\parallel} + 2\sigma_{\perp}]$$

nuclear Larmor frequency δ :

$$\nu_L = \frac{\gamma \mathcal{B}_{\text{loc}}}{2\pi} = (1 - \sigma) \frac{\gamma \mathcal{B}_0}{2\pi}$$

chemical shift:

$$\delta = \frac{\nu - \nu^0}{\nu^0} \times 10^6$$

$$\left\{ \begin{array}{l} \sigma = \sigma_D + \sigma_P \\ \sigma_D = \frac{4\pi e^2}{3mc^2} \int_0^{\infty} r \rho(r) dr \end{array} \right. \quad (46)$$

σ_D diamagnetic term:

positive, e^{-1} circulation shields the nucleus

σ_P paramagnetic term :

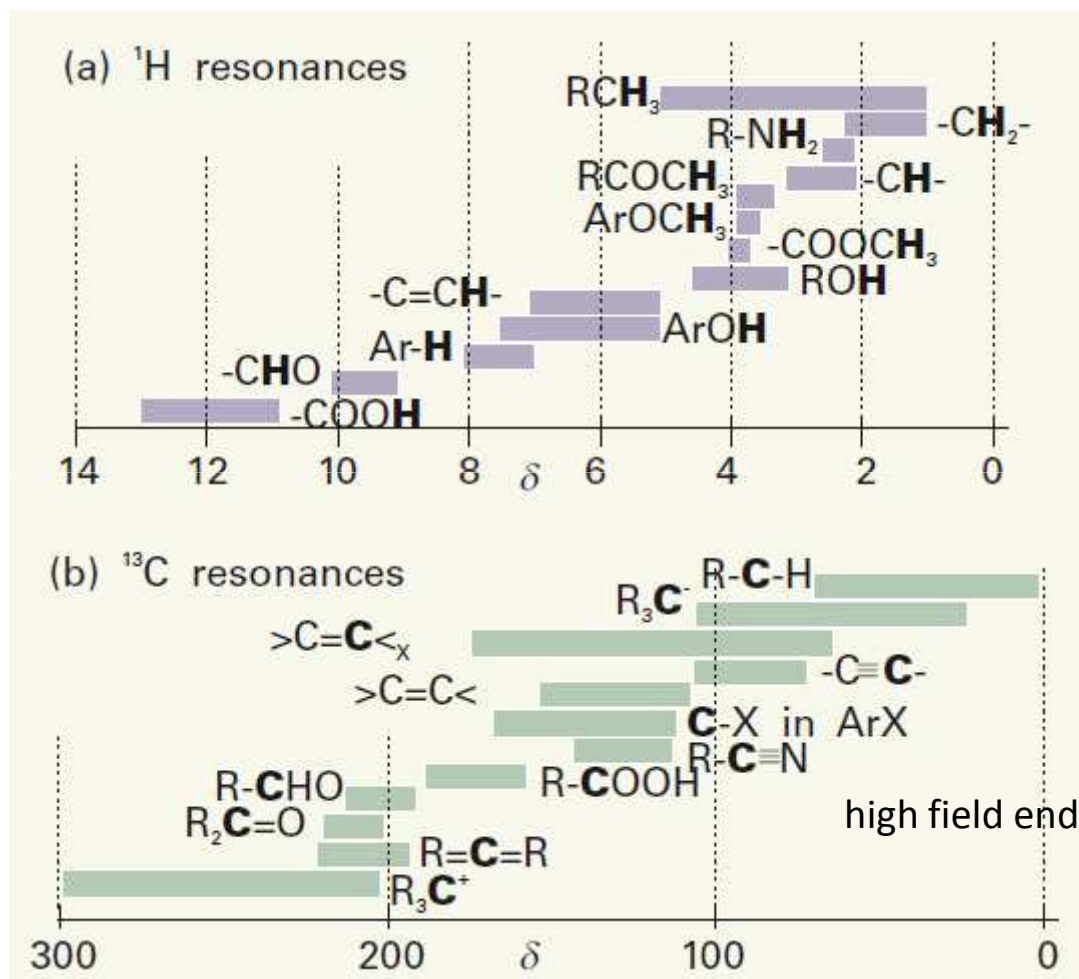
negative, non spherical symmetry about the nucleus (p and d el)

$$(47)$$

The chemical shift

$$\delta = \frac{(1 - \sigma)B_0 - (1 - \sigma^0)B_0}{(1 - \sigma^0)B_0} \times 10^6$$

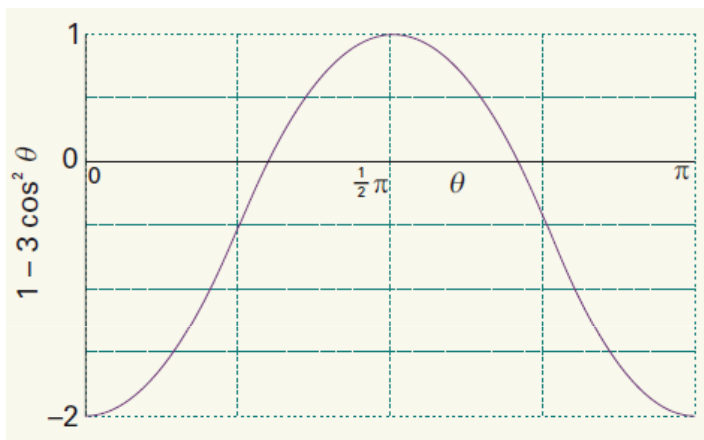
$$= \frac{\sigma^0 - \sigma}{1 - \sigma^0} \times 10^6 \approx (\sigma^0 - \sigma) \times 10^6$$



^{13}C : greater the range of shieldings.

Chemical shift: Neighbouring group contributions

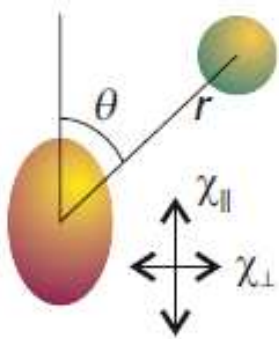
H-X molecule, X diamagnetic:
 induced magnetic field



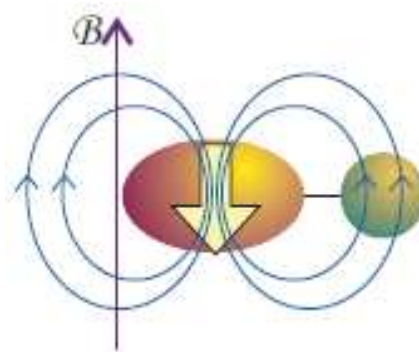
the change in proton shielding :

$$\sigma(\text{neighbour}) \propto (\chi_{\parallel} - \chi_{\perp}) \left(\frac{1 - 3 \cos^2 \theta}{r^3} \right) \quad (48)$$

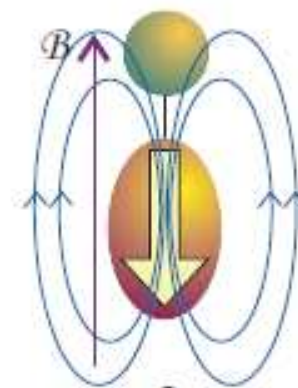
χ_{\parallel} and χ_{\perp} are both negative



$\theta = 0$

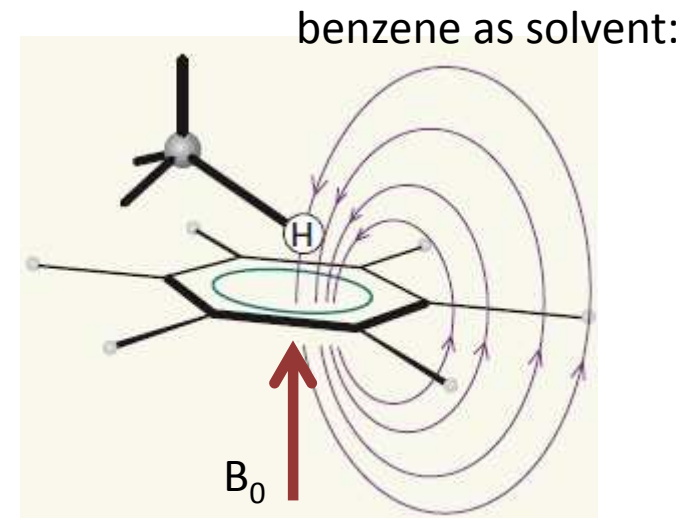
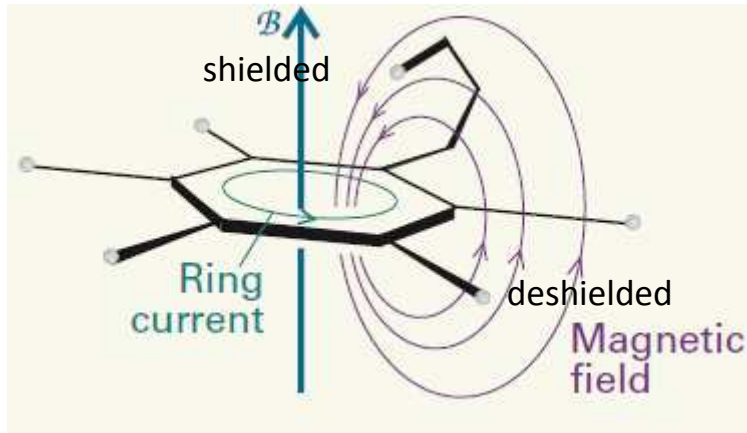


shielding

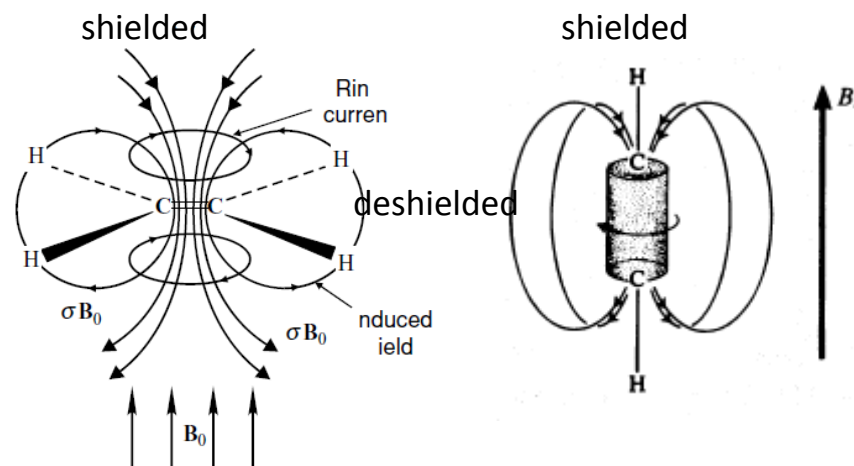
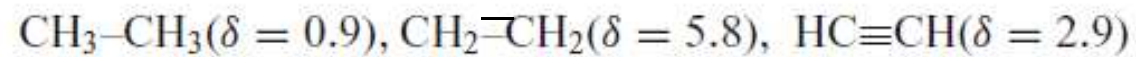


deshielding

Chemical shift: Ring current



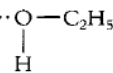

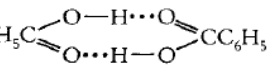


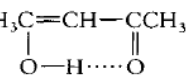
The effect of multiple bonds on the chemical shift:

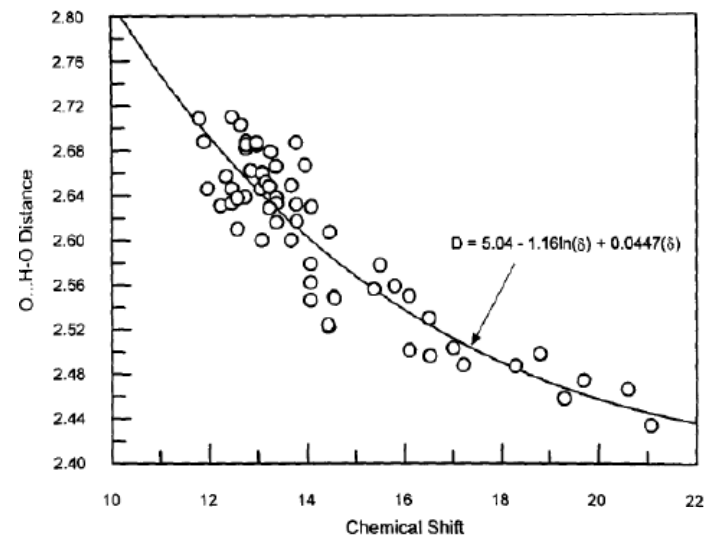


Chemical shift: Hydrogen Bonding

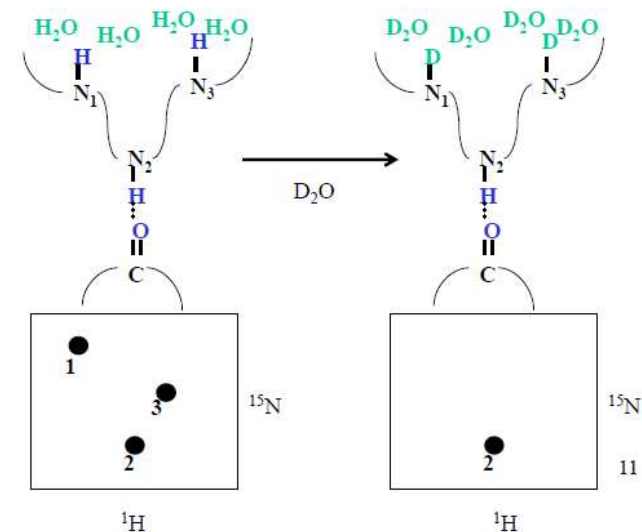
A polar molecule dissolved in a dielectric medium: "reaction field," that reduce the shielding around a proton in the solute.

A-H - - - B

Compound	$\delta(\text{bonded})^b$	$\delta(\text{bonded}) - \delta(\text{free})$
<chem>C2H5OH...O-C2H5</chem> 	5.3	4.6
<chem>C6H5OH...O=P(OC2H5)3</chem>	8.7	4.3
<chem>Cl3CH...O=C(CH3)2</chem>	8.0	0.7
<chem>Cl3CH...C6H6</chem> 	6.4	-0.9
<chem>C6H5C(=O)OH...O=C(C6H5)2</chem> 	14.0	7.8
<chem>C6H5NH2...N(C6H5)2</chem> 	5.3	2.0
<chem>C6H5NH2...O=S(CH3)2</chem>	5.0	1.7
<chem>C6H5SH...O=C-N(CH3)2</chem> 	3.8	0.5
<chem>CH3C(=O)CH=C(CH3)2</chem> 	15.5	—

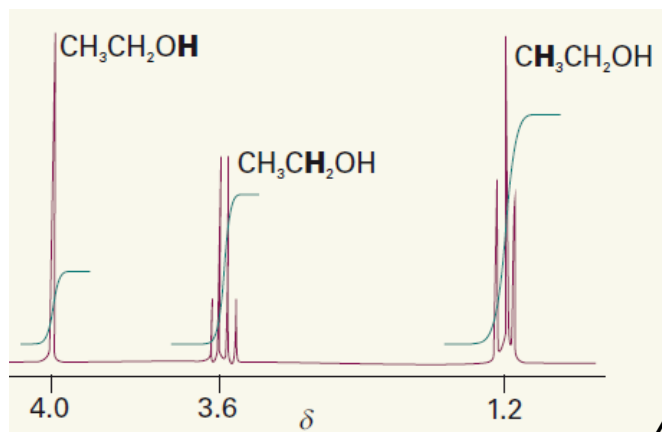


H/D exchange



Intermolecular H-bonds between small molecules: made and broken very rapidly

The fine structure: scalar coupling



The ^1H -NMR spectrum of ethanol.

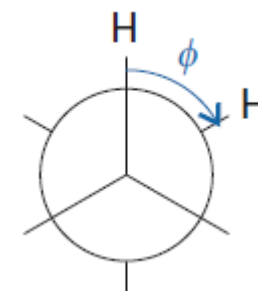
J_{XY} : $J < 0$ spins are parallel or
 $J > 0$ spins are antiparallel

Karplus formula 3J :

$$J = A + B \cos \phi + C \cos 2\phi$$

A , B , and C empirical constants:

+7 Hz, -1 Hz, and +5 Hz, for an HCCH fragment.



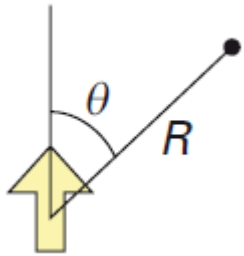
$^1J_{CH}$: 120 to 250 Hz; $^2J_{CH}$: -10 and +20 Hz

Couplings Involving Heteronuclear (^{13}C or ^{15}N) Spins		Proton-Proton Couplings	
C-N	14 Hz	H-C-H	-12 to -15 Hz
C-C	35 Hz	H-C-C-H	2-14 Hz
H-N	92 Hz	H-C=C-H	10 (cis)/17 (trans)
H-C	130 Hz	H-N-C-H	1-10 Hz
H-C-C	5 Hz (two bond coupling)		(3 Hz α -helix) (10 Hz β -strand)

J_{CH} depends on the hybridization of the C atom

$^1J_{CH}/\text{Hz}$:	sp	sp^2	sp^3
	250	160	125

The origin of spin-spin coupling



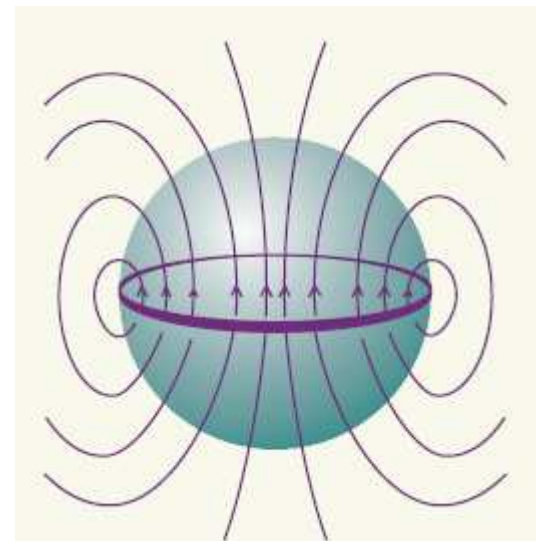
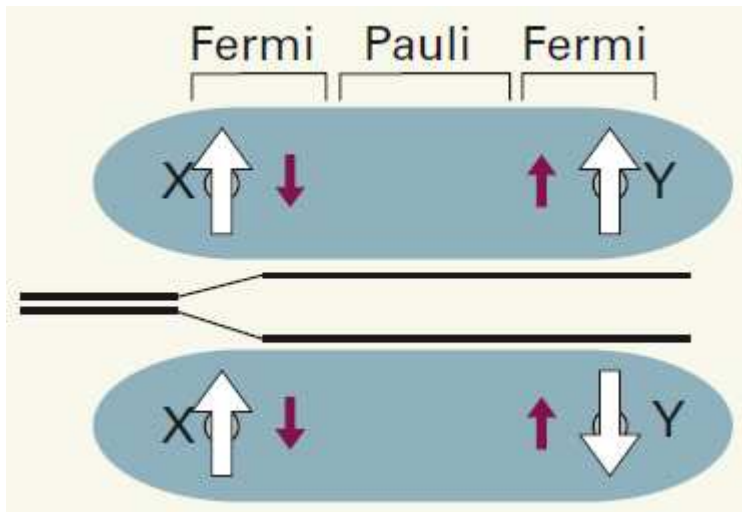
$$\mathcal{B}_{\text{nuc}} = -\frac{\gamma \hbar \mu_0}{4\pi R^3} (1 - 3\cos^2\theta) m_I \sim 0.1 \text{ mT when } R = 0.3 \text{ nm: splitting } 10 \text{ MHz (solids)}$$

averages to 0 in liquids

Spin-spin coupling in molecules in solution: based on **polarization mechanism**, in which the interaction is transmitted through the bonds (X and Y are spin 1/2 nuclei).

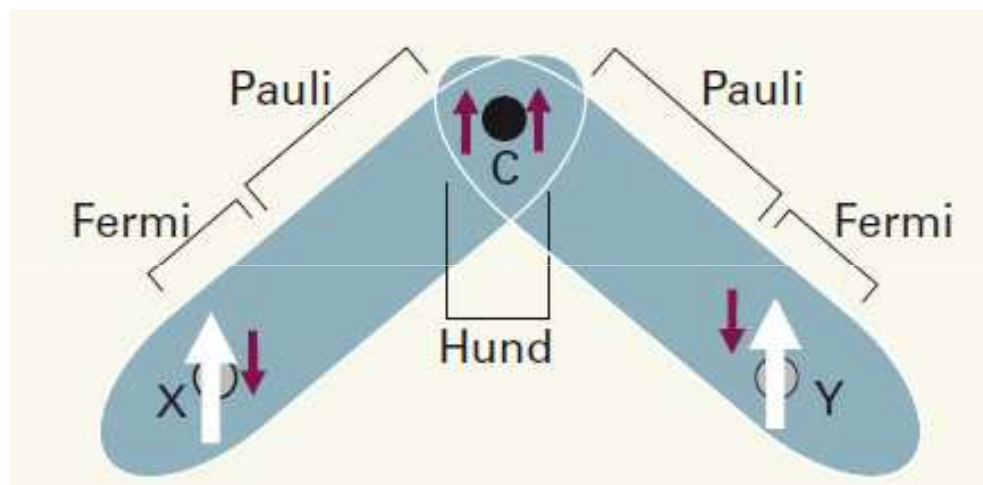
$^1J_{\text{CH}}$

Fermi contact interaction



The origin of spin–spin coupling

${}^2J_{XY}$: H-C-H



The coupling of nuclear spin to electron spin by the Fermi contact interaction is most important for proton spins, but not for other nuclei (dipolar coupling).

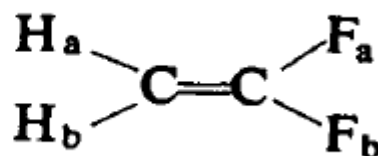
Equivalent nuclei

difluoromethane



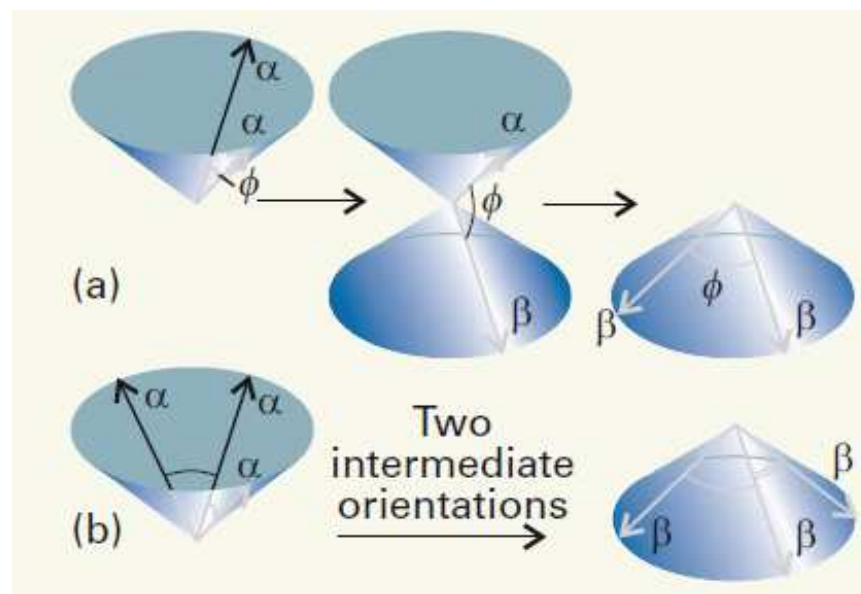
chemically equivalent
magnetically equivalent

1,1-difluoroethylene

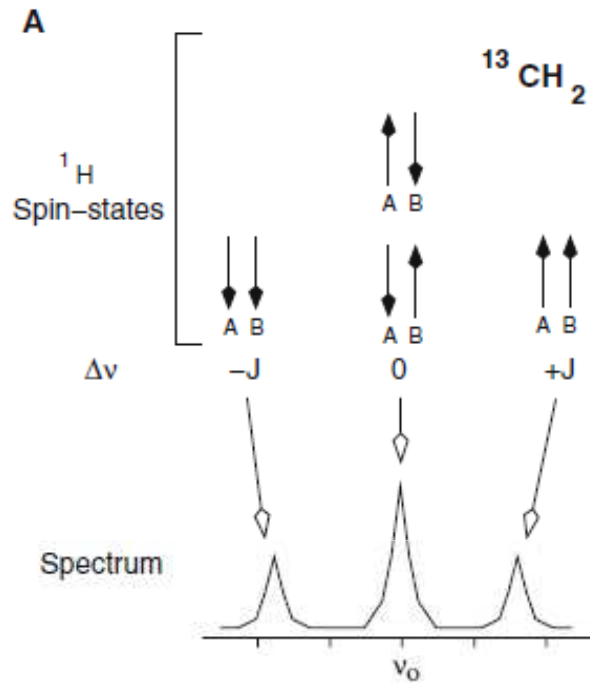


chemically equivalent
not magnetically equivalent

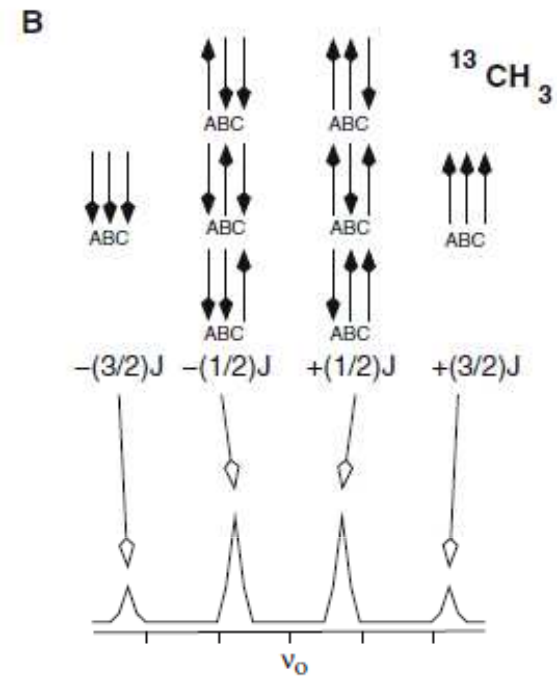
The coupling of chemically equivalent nuclei has no effect on the appearance of the spectrum.



Coupling to Multiple Spins

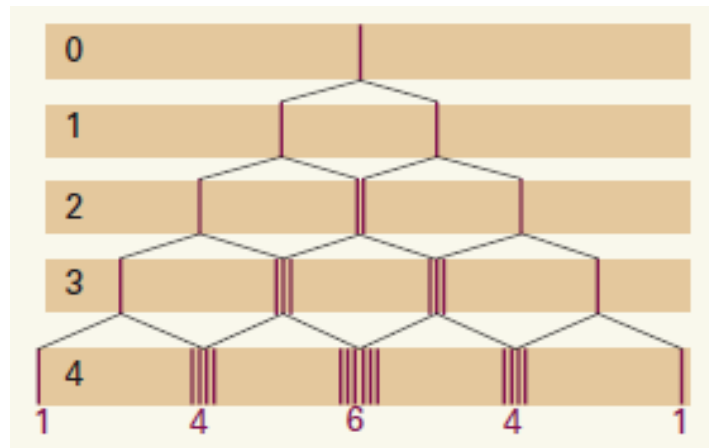


intensity ratio of 1:2:1



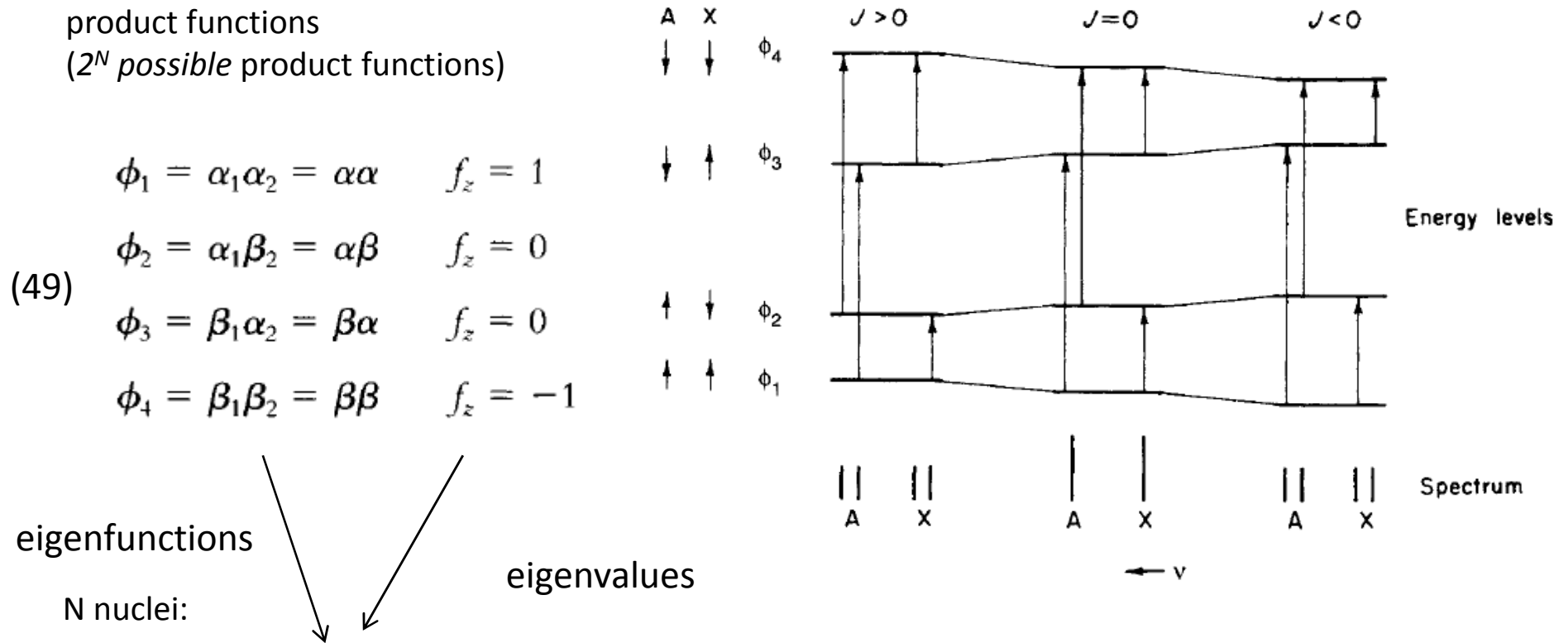
intensity ratio of 1:3:3:1

AX_n
Pascal's triangle:
binomial distribution



The AX system

AX: two coupled spins that differ greatly in their resonance frequencies ($\Delta\nu > J$)
 couplings between heteronuclear spins: J_{NH} , J_{CH} and J_{NC}



$$(50) \quad F_z = (I_z)_1 + (I_z)_2 + \dots = \sum_{i=1}^N (I_z)_i = \sum_{i=1}^N I_{zi}$$

The AX system

N-spin system:

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} \quad (51)$$

$$\begin{aligned}
 \mathcal{H}^{(0)} &= -\sum_{i=1}^N \frac{\gamma_i}{2\pi} B_0 (1 - \sigma_i) I_{zi} & \mathcal{H}^{(1)} &= \sum_{i=1}^N \sum_{j=i}^N J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j \\
 (52) \quad &= -\sum_{i=1}^N \nu_i I_{zi} & &= \sum_{i=1}^N \sum_{j=i}^N J_{ij} [I_{xi} I_{xj} + I_{yi} I_{yj} + I_{zi} I_{zj}] \quad (53)
 \end{aligned}$$

the secular equation

$$|\mathcal{H}_{mn} - E\delta_{mn}| = 0$$

$$\begin{vmatrix}
 \mathcal{H}_{11} - E & \mathcal{H}_{12} & \mathcal{H}_{13} & \cdots \\
 \mathcal{H}_{21} & \mathcal{H}_{22} - E & \mathcal{H}_{23} & \cdots \\
 \mathcal{H}_{31} & \mathcal{H}_{32} & \mathcal{H}_{33} - E & \cdots \\
 \cdots & \cdots & \cdots & \cdots
 \end{vmatrix} = 0 \quad (54)$$

$$\mathcal{H}_{mn} = \langle \phi_m | \mathcal{H} | \phi_n \rangle \quad (55)$$

The uncoupled AB system (J = 0)

Diagonal matrix elements

$$\mathcal{H}_{11} = \langle \phi_1 | \mathcal{H}^{(0)} | \phi_1 \rangle \quad (55)$$

$$\begin{aligned} &= -\langle \alpha_A \beta_B | \nu_A I_{zA} + \nu_B I_{zB} | \alpha_A \beta_B \rangle \\ &= -\nu_A \langle \alpha_A \alpha_B | I_{zA} | \alpha_A \alpha_B \rangle - \nu_B \langle \alpha_A \alpha_B | I_{zB} | \alpha_A \alpha_B \rangle \\ &= -\nu_A \langle \alpha_A | I_{zA} | \alpha_A \rangle \langle \alpha_B | \alpha_B \rangle - \nu_B \langle \alpha_A | \alpha_A \rangle \langle \alpha_B | I_{zB} | \alpha_B \rangle \\ &= -\nu_A (1/2)(1) - \nu_B (1)(1/2) = -1/2(\nu_A + \nu_B) \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{22} &= -1/2(\nu_A - \nu_B) \\ \mathcal{H}_{33} &= -1/2(-\nu_A + \nu_B) \\ \mathcal{H}_{44} &= 1/2(\nu_A + \nu_B) \end{aligned} \quad (56)$$

Off-diagonal matrix elements:

$$\begin{aligned} \mathcal{H}_{12} &= \langle \phi_1 | \mathcal{H}^{(0)} | \phi_2 \rangle \\ &= -\langle \alpha_A \alpha_B | \nu_A I_{zA} + \nu_B I_{zB} | \alpha_A \beta_B \rangle \\ &= -\nu_A \langle \alpha_A \alpha_B | I_{zA} | \alpha_A \beta_B \rangle - \nu_B \langle \alpha_A \alpha_B | I_{zB} | \alpha_A \beta_B \rangle \\ &= -\nu_A \langle \alpha_A | I_{zA} | \alpha_A \rangle \langle \alpha_B | \beta_B \rangle - \nu_B \langle \alpha_A | \alpha_A \rangle \langle \alpha_B | I_{zB} | \beta_B \rangle \\ &= -\nu_A (1/2)(0) - \nu_B (1)(0) = 0 \end{aligned}$$

Solutions of the secular equation:

$$\begin{aligned} E_1 &= \mathcal{H}_{11} = -1/2(\nu_A + \nu_B) \\ E_2 &= \mathcal{H}_{22} = -1/2(\nu_A - \nu_B) \\ E_3 &= \mathcal{H}_{33} = 1/2(\nu_A - \nu_B) \\ E_4 &= \mathcal{H}_{44} = 1/2(\nu_A + \nu_B) \end{aligned} \quad (57)$$

selection rule $\Delta F_z = \pm 1$

Hamiltonian is diagonal in the original Φ_i basis set: Φ_i are the true wave functions

The coupled AB system

The product functions Φ_n are eigenfunctions of F_z

$$F_z \mathcal{H} - \mathcal{H} F_z = 0$$

f_m and f_n are eigenvalues of the operator F_z :

$$F\phi_m = f_m\phi_m \quad F\phi_n = f_n\phi_n$$

$$(f_m - f_n)\langle\phi_m|\mathcal{H}|\phi_n\rangle = 0$$

$$(f_m - f_n)\mathcal{H}_{mn} = 0$$

$$f_m - f_n \neq 0, \mathcal{H}_{mn} = 0.$$

$$\phi_1 = \alpha_1\alpha_2 = \alpha\alpha \quad f_z = 1$$

$$\phi_2 = \alpha_1\beta_2 = \alpha\beta \quad f_z = 0$$

$$\phi_3 = \beta_1\alpha_2 = \beta\alpha \quad f_z = 0$$

$$\phi_4 = \beta_1\beta_2 = \beta\beta \quad f_z = -1$$

only \mathcal{H}_{23} and \mathcal{H}_{32} are nonzero (

$$\mathcal{H}_{23} = \mathcal{H}_{32}.$$

The secular equation

$$\begin{vmatrix} \mathcal{H}_{11} - E & 0 & 0 & 0 \\ 0 & \mathcal{H}_{22} - E & \mathcal{H}_{23} & 0 \\ 0 & \mathcal{H}_{32} & \mathcal{H}_{33} - E & 0 \\ 0 & 0 & 0 & \mathcal{H}_{44} - E \end{vmatrix} = 0 \quad (58)$$

The coupled AB system

$$\begin{aligned}
 \mathcal{H}_{11}^{(1)} &= \langle \phi_1 | \mathcal{H}^{(1)} | \phi_1 \rangle & \mathcal{H}_{22}^{(1)} &= -\frac{1}{4} J_{AB} \\
 &= J_{AB} \langle \alpha_A \alpha_B | I_{xA} I_{xB} + I_{yA} I_{yB} + I_{zA} I_{zB} | \alpha_A \alpha_B \rangle & \mathcal{H}_{33}^{(1)} &= -\frac{1}{4} J_{AB} \\
 &= J_{AB} [\langle \alpha_A | I_{xA} | \alpha_A \rangle \langle \alpha_B | I_{xB} | \alpha_B \rangle + \langle \alpha_A | I_{yA} | \alpha_A \rangle \langle \alpha_B | I_{yB} | \alpha_B \rangle & \mathcal{H}_{44}^{(1)} &= \frac{1}{4} J_{AB} \\
 &\quad + \langle \alpha_A | I_{zA} | \alpha_A \rangle \langle \alpha_B | I_{zB} | \alpha_B \rangle] & & \\
 &= J_{AB} [0 + 0 + (\frac{1}{2})(\frac{1}{2})] & & \\
 &= \frac{1}{4} J_{AB} & &
 \end{aligned} \tag{59}$$

The lone nonzero off-diagonal element

$$\begin{aligned}
 \mathcal{H}_{23}^{(1)} &= \langle \phi_2 | \mathcal{H}^{(1)} | \phi_3 \rangle \\
 &= J_{AB} \langle \alpha_A \beta_B | I_{xA} I_{xB} + I_{yA} I_{yB} + I_{zA} I_{zB} | \beta_A \alpha_B \rangle \\
 &= J_{AB} [\langle \alpha_A | I_{xA} | \beta_A \rangle \langle \beta_B | I_{xB} | \alpha_B \rangle + \langle \alpha_A | I_{yA} | \beta_A \rangle \langle \beta_B | I_{yB} | \alpha_B \rangle \\
 &\quad + \langle \alpha_A | I_{zA} | \beta_A \rangle \langle \beta_B | I_{zB} | \alpha_B \rangle] \\
 &= J_{AB} [(\frac{1}{2})(\frac{1}{2}) + (\frac{1}{2}i)(-\frac{1}{2}i) + 0] \\
 &= \frac{1}{2} J_{AB}
 \end{aligned}$$

The complete matrix elements :

$$\begin{aligned}
 \mathcal{H}_{11} &= -\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{4} J_{AB} \\
 \mathcal{H}_{22} &= -\frac{1}{2}(\nu_A - \nu_B) - \frac{1}{4} J_{AB} \\
 \mathcal{H}_{33} &= \frac{1}{2}(\nu_A - \nu_B) - \frac{1}{4} J_{AB} \\
 \mathcal{H}_{44} &= \frac{1}{2}(\nu_A + \nu_B) + \frac{1}{4} J_{AB} \\
 \mathcal{H}_{23} &= \frac{1}{2} J_{AB}
 \end{aligned} \tag{60}$$

The coupled AB system

The energies

$$\begin{aligned}
 E_1 &= -\frac{1}{2}[\nu_A + \nu_B] + \frac{1}{4}J_{AB} && (\nu_A - \nu_B) \gg J_{AB} \\
 E_2 &= -\frac{1}{2}[(\nu_A - \nu_B)^2 + J_{AB}^2]^{1/2} - \frac{1}{4}J_{AB} && \text{AX system} \\
 E_3 &= \frac{1}{2}[(\nu_A - \nu_B)^2 + J_{AB}^2]^{1/2} - \frac{1}{4}J_{AB} \\
 E_4 &= \frac{1}{2}[\nu_A + \nu_B] + \frac{1}{4}J_{AB}
 \end{aligned}
 \tag{61}$$

The wave functions $\Psi_1 - \Psi_4$:

$$\Psi = \sum_{i=1}^n c_i |u_i\rangle$$

$$\psi_1 = \phi_1$$

$$\begin{aligned}
 \psi_2 &= \frac{1}{(1 + Q^2)^{1/2}} (\phi_2 + Q\phi_3) \\
 \psi_3 &= \frac{1}{(1 + Q^2)^{1/2}} (-Q\phi_2 + \phi_3)
 \end{aligned}
 \tag{65}$$

$$\psi_4 = \phi_4$$

$$Q = \frac{J_{AB}}{(\nu_A - \nu_B) + [(\nu_A - \nu_B)^2 + J_{AB}^2]^{1/2}}$$

N non-interacting nuclei:

$$\Delta m_i = \pm 1 \quad \text{for one nucleus}
 \tag{63}$$

$$\Delta m_j = 0 \quad \text{for all others}$$

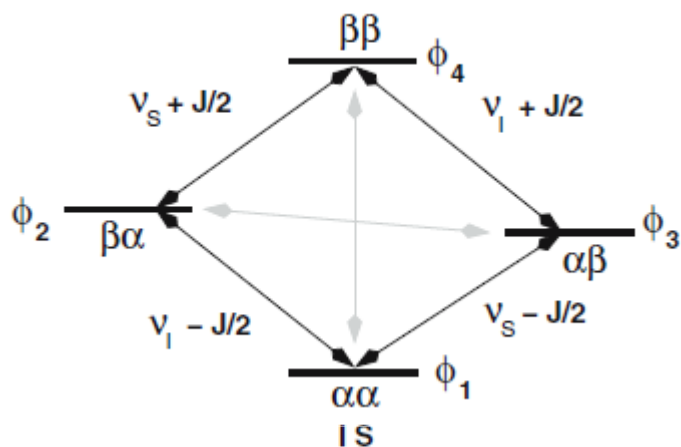
For coupled nuclei

$$\Delta f_z = \pm 1
 \tag{64}$$

The coupled AB system

four allowed transitions

$$\phi_3 \rightarrow \phi_1, \phi_4 \rightarrow \phi_2, \phi_4 \rightarrow \phi_3, \text{ and } \phi_2 \rightarrow \phi_1.$$



$$\nu_1 = E_4 - E_2 = \frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}[(\nu_A - \nu_B)^2 + J_{AB}^2]^{1/2} + \frac{1}{2}J_{AB}$$

$$\nu_2 = E_3 - E_1 = \frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}[(\nu_A - \nu_B)^2 + J_{AB}^2]^{1/2} - \frac{1}{2}J_{AB}$$

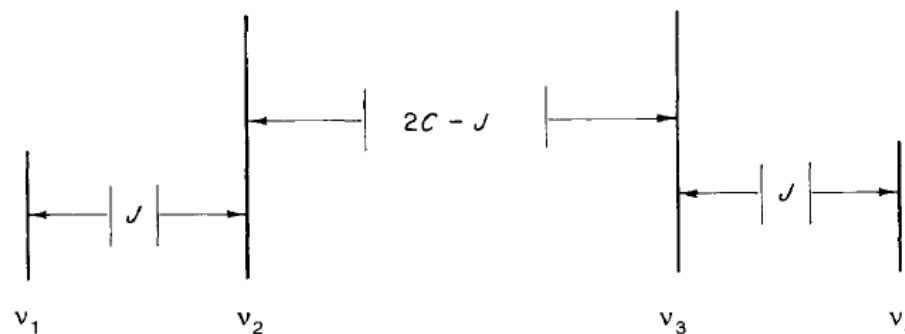
$$\nu_3 = E_4 - E_3 = \frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}[(\nu_A - \nu_B)^2 + J_{AB}^2]^{1/2} + \frac{1}{2}J_{AB}$$

$$\nu_4 = E_2 - E_1 = \frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}[(\nu_A - \nu_B)^2 + J_{AB}^2]^{1/2} - \frac{1}{2}J_{AB}$$

$$C = \frac{1}{2}[(\nu_A - \nu_B)^2 + J^2]^{1/2} \quad (65)$$

Line	Transition	Frequency (Hz) ^a	Relative intensity
1	$T_{2 \rightarrow 4}$	$C + \frac{1}{2}J$	$1 - \frac{J}{2C}$
2	$T_{1 \rightarrow 3}$	$C - \frac{1}{2}J$	$1 + \frac{J}{2C}$
3	$T_{3 \rightarrow 4}$	$-C + \frac{1}{2}J$	$1 + \frac{J}{2C}$
4	$T_{1 \rightarrow 2}$	$-C - \frac{1}{2}J$	$1 - \frac{J}{2C}$

^aReferred to the center of the four-line pattern, $\frac{1}{2}(\nu_A + \nu_B)$.

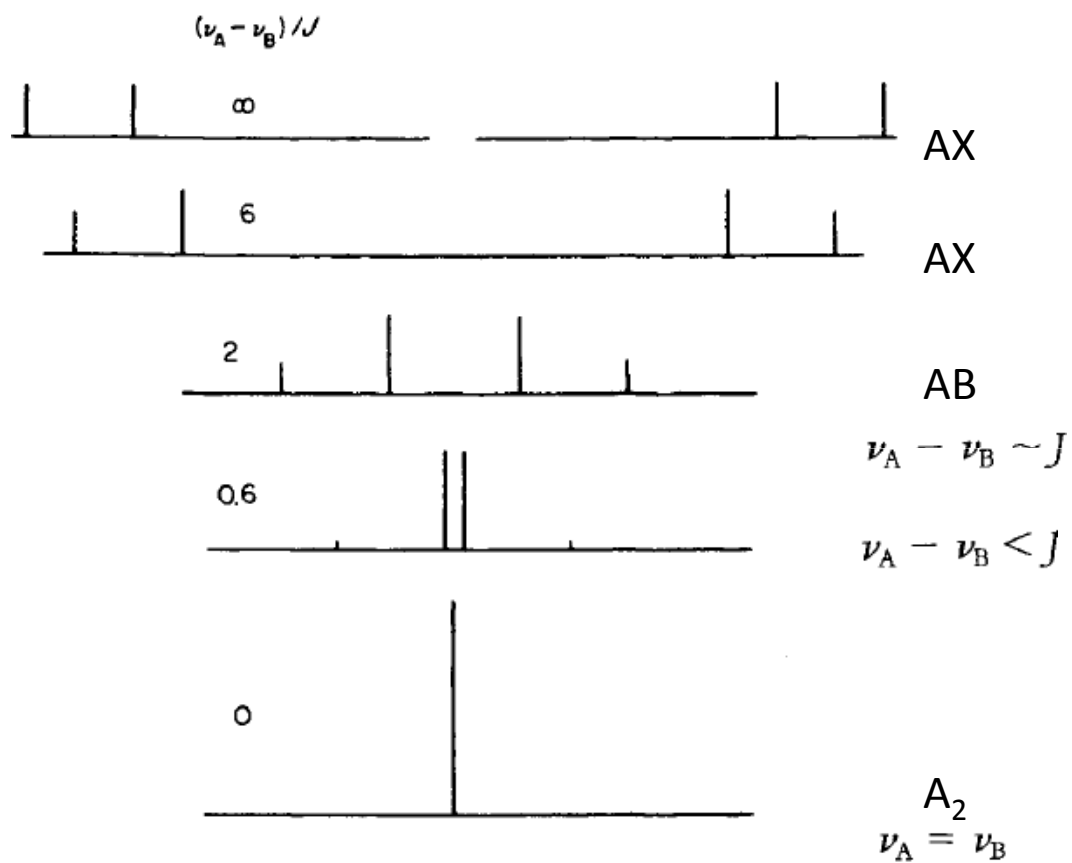


$$|\nu_A - \nu_B| = [4C^2 - J^2]^{1/2}$$

$$= [(2C - J)(2C + J)]^{1/2} \quad (66)$$

$$= [(\nu_2 - \nu_3)(\nu_1 - \nu_4)]^{1/2}$$

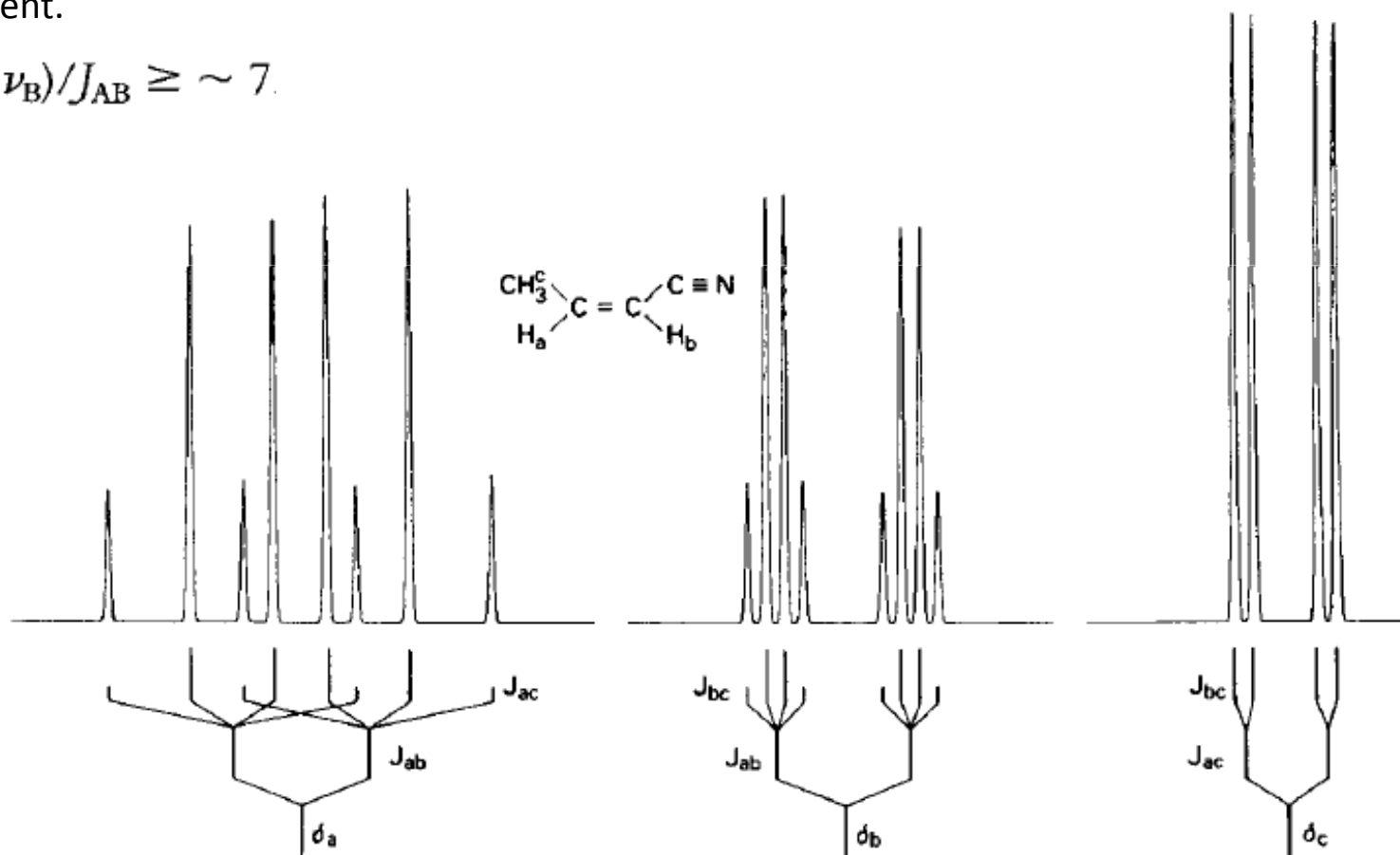
AX, AB, and A₂ Spectra



“First-order” spectra

1. The chemical shift difference in hertz between nuclei (or groups of nuclei) must be much larger than the spin coupling between them.
2. Coupling must involve groups of nuclei that are magnetically equivalent, not just chemically equivalent.

$$(\nu_A - \nu_B)/J_{AB} \geq \sim 7.$$



Spin decoupling: double resonance

- „cleans“ NMR spectra
- enhances sensitivity

