Fyzikálně-chemické základy **n**ukleární **m**agnetické **r**ezonance

James Keeler: Understanding NMR Spectroscopy
University of Cambridge, Department of Chemistry
2002

NMR a elektromagnetické spektrum

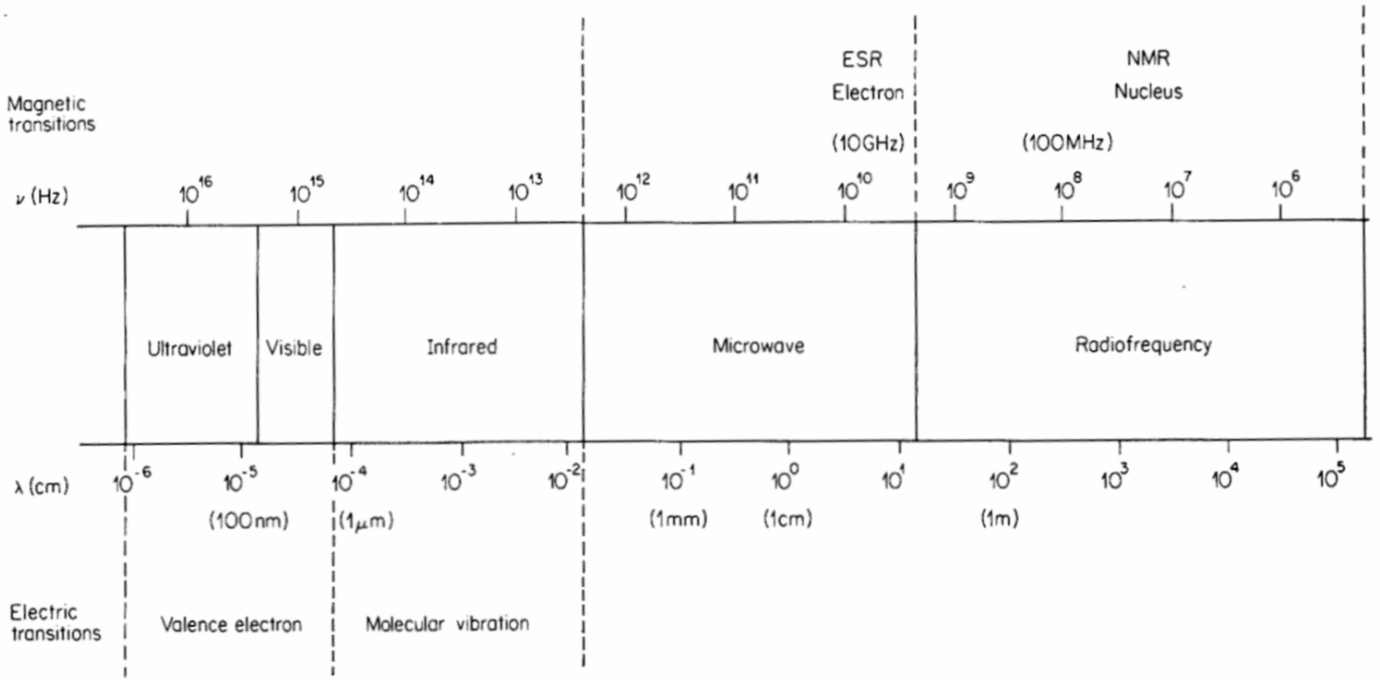
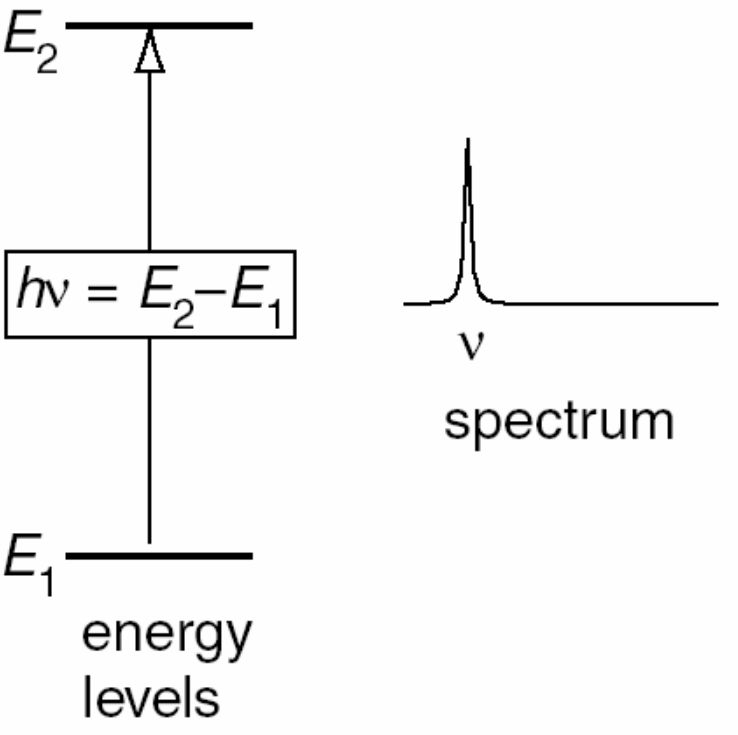


Figure 1.2 Spectral regions of the electromagnetic spectrum of interest in biological investigations

NMR a energiové hladiny

$$\Delta E = h\nu$$



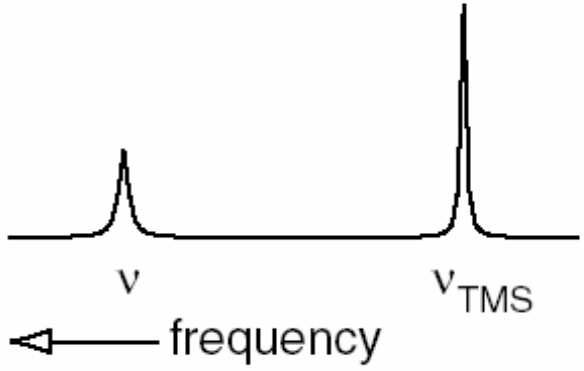
h - Planckova konstanta = $6{,}626.10^{-34}$ J.s

NMR a energiové hladiny

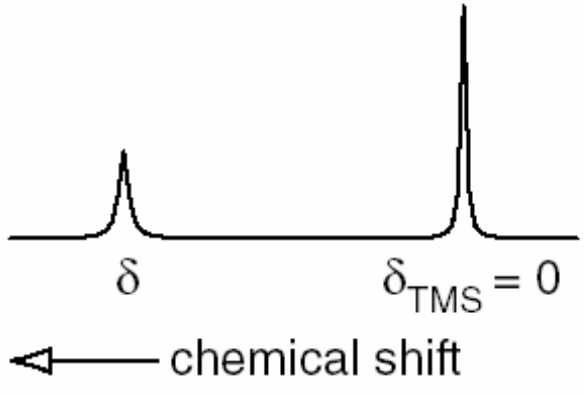
Chemický posun

$$\delta = \frac{\nu - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}}.$$

$$\delta_{\mathrm{ppm}} = 10^6 \times \frac{\nu - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}}.$$



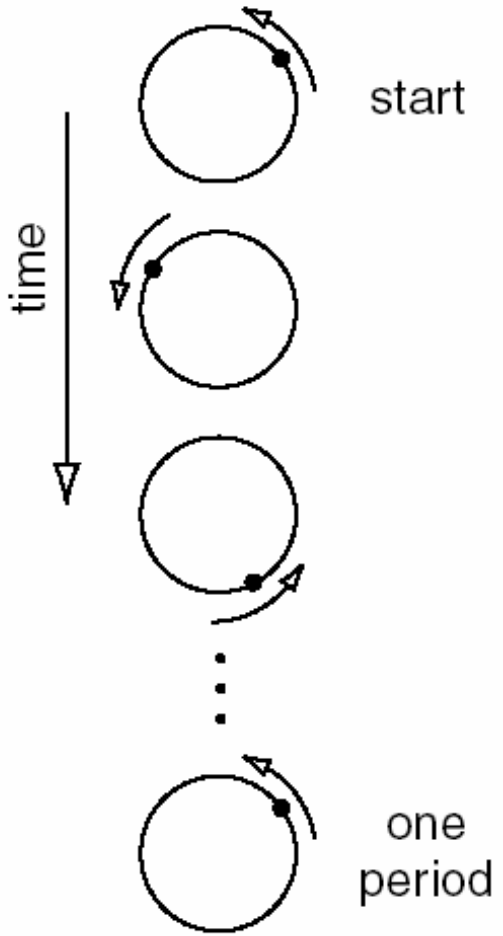
$$(\delta_2 - \delta_1) = 10^6 \times \frac{\nu_2 - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}} - 10^6 \times \frac{\nu_1 - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}}$$
$$= 10^6 \times \frac{\nu_2 - \nu_1}{\nu_{\mathrm{TMS}}}.$$



$$(\nu_2 - \nu_1) = 10^{-6} \times \nu_{\mathrm{TMS}} \times (\delta_2 - \delta_1).$$

NMR a energiové hladiny

Rotační frekvence a energie



$$\nu = \frac{1}{\tau}.$$

$$\omega = \frac{2\pi}{\tau}.$$

$$\nu = \frac{\omega}{2\pi} \quad \text{or} \quad \omega = 2\pi\nu.$$

$$E = h\frac{\omega}{2\pi}$$
$$= \hbar\omega$$

NMR a energiové hladiny

Nukleární spin a spinové stavy

$I = k * ½$, k je celé číslo 0, 1, 2 …. spinové kvantové číslo

m = -I, -I+1, -I+2 ……I-2, I-1, I magnetické kvantové číslo

pro I = ½ m = ½ α stav
m = –½ β stav

Pro 2 spiny s I= ½ existují 4 možné kombinace stavů αα, αβ, βα a ββ
Pro 3 spiny s I= ½ existuje 8 možností kombinace stavů
ααα, ααβ, αβα, βαα, αββ, βαβ, ββα, a βββ

NMR a energiové hladiny

$E_m = m * \nu_{0,1}$ ← pořadové číslo spinu

ν_0 - Larmorova frekvence

$E_\alpha = + ½ * \nu_{0,1}$ $E_\beta = - ½ * \nu_{0,1}$

$$\nu_{0,1} = -\frac{1}{2\pi}\gamma_1(1+\delta_1)B_0$$

$$\omega_0 = -\gamma(1+\delta)B_0$$

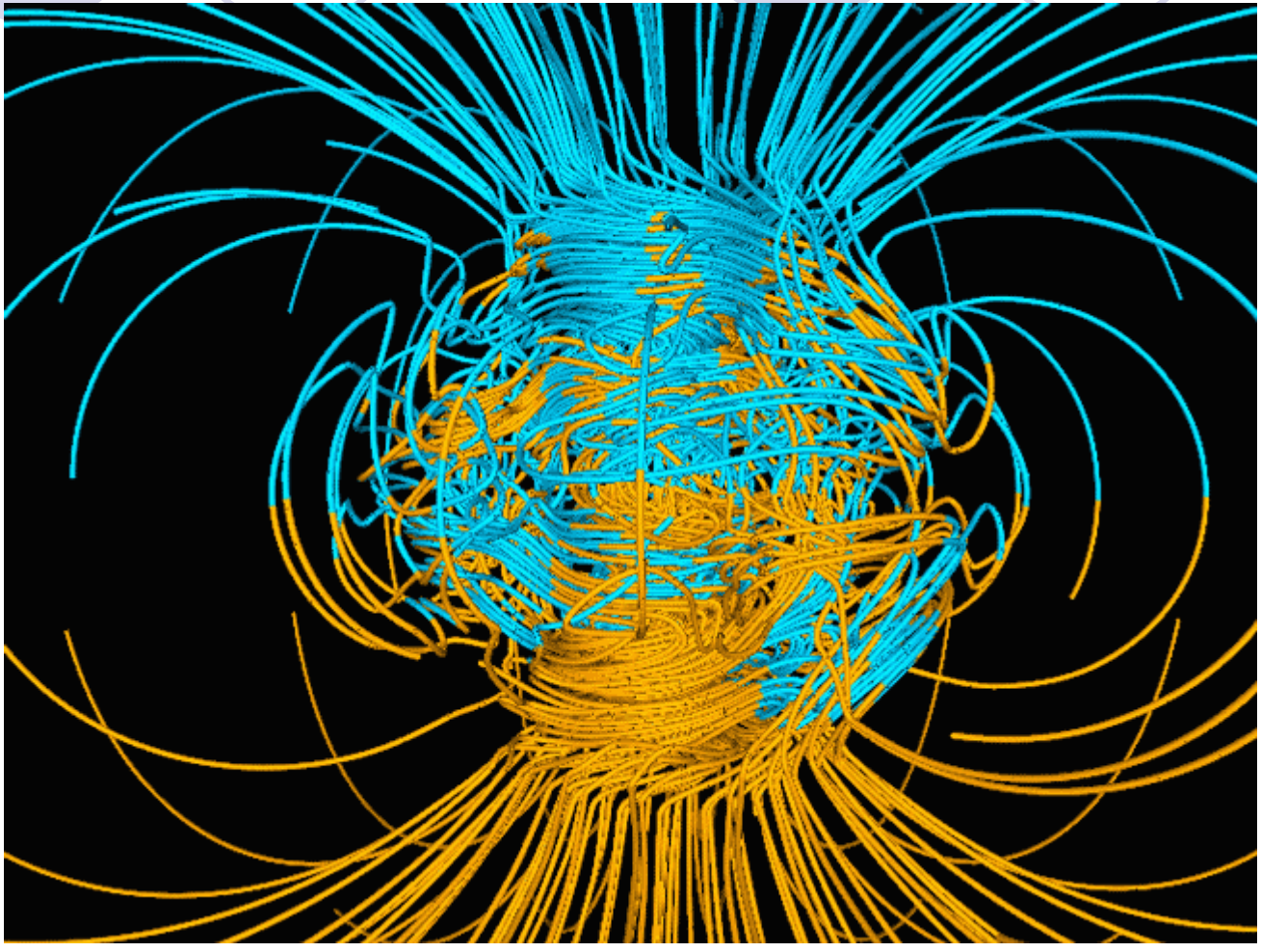
γ - magnetogyrická konstanta (poměr) [rad. $s^{-1}.T^{-1}$]

pro ^1H $\gamma = +2{,}67 \times 10^8$ rad. $s^{-1}.T^{-1}$ = 42 494 369 $s^{-1}.T^{-1}$

Při B0 = 4.7 T

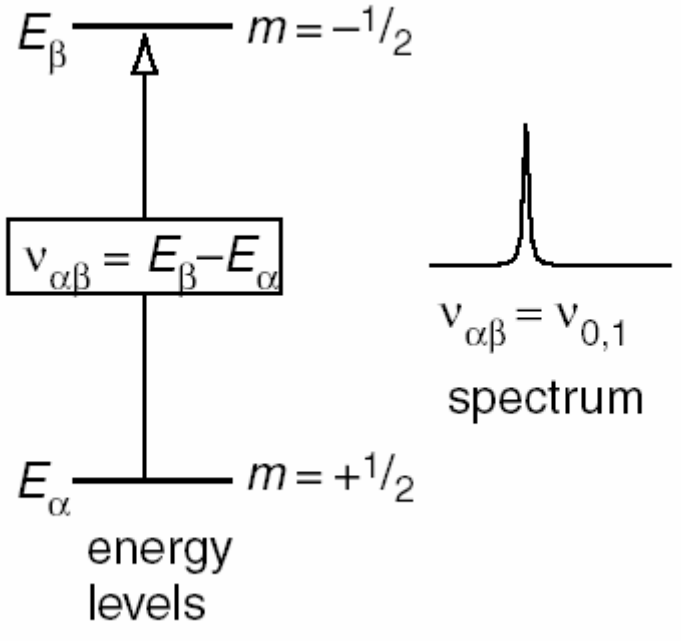
$\nu_0 = -200 \times 10^6$ Hz a $\omega_0 = -1{,}225 \times 10^9$ rad.s^{-1}

Zemské magnetické pole B_o = 40 mT, ν_0 = -1.7 MHz



NMR a energiové hladiny

Spektrum

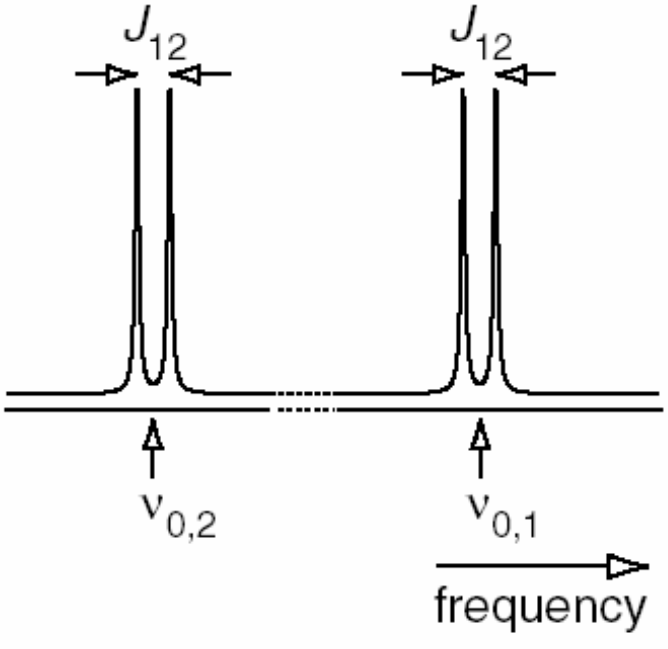


$$\begin{aligned}\triangle m &= m(\text{initial state}) - m(\text{final state}) \\ &= \pm 1.\end{aligned}$$

$$\begin{aligned}\nu_{\alpha\beta} &= E_\beta - E_\alpha \\ &= -\tfrac{1}{2}\nu_{0,1} - (+\tfrac{1}{2}\nu_{0,1}) \\ &= -\nu_{0,1}.\end{aligned}$$

NMR a energiové hladiny

Dva spiny



$$\nu_{0,1} = -\frac{1}{2\pi}\gamma_1(1+\delta_1)B_0$$

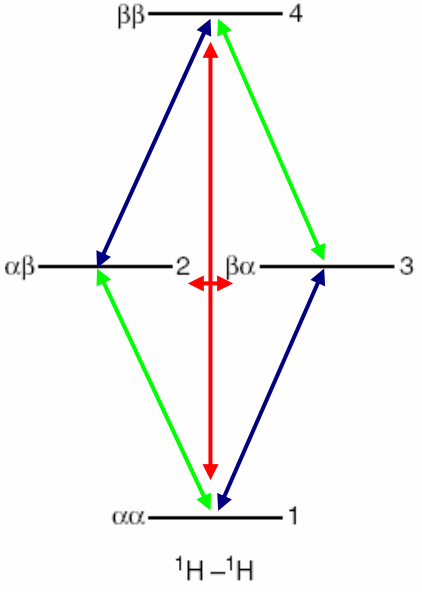
$$\nu_{0,2} = -\frac{1}{2\pi}\gamma_2(1+\delta_2)B_0.$$

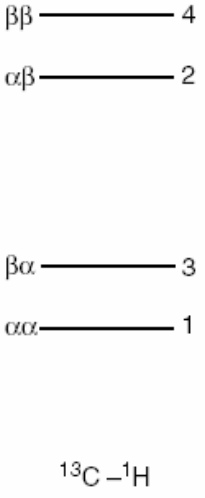
number	spin states	energy
1	$\alpha\alpha$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$
2	$\alpha\beta$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
3	$\beta\alpha$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
4	$\beta\beta$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$

$$E_{m_1 m_2} = m_1\nu_{0,1} + m_2\nu_{0,2} + m_1 m_2 J_{12}$$

NMR a energiové hladiny

Dva spiny





$$M = m_1 + m_2.$$

number	spin states	M
1	$\alpha\alpha$	1
2	$\alpha\beta$	0
3	$\beta\alpha$	0
4	$\beta\beta$	−1

Výběrové pravidlo $\Delta M = \pm 1$

Dovolené přechody mezi

1-3 a 2-4, 1-2 a 3-4,

NMR a energiové hladiny

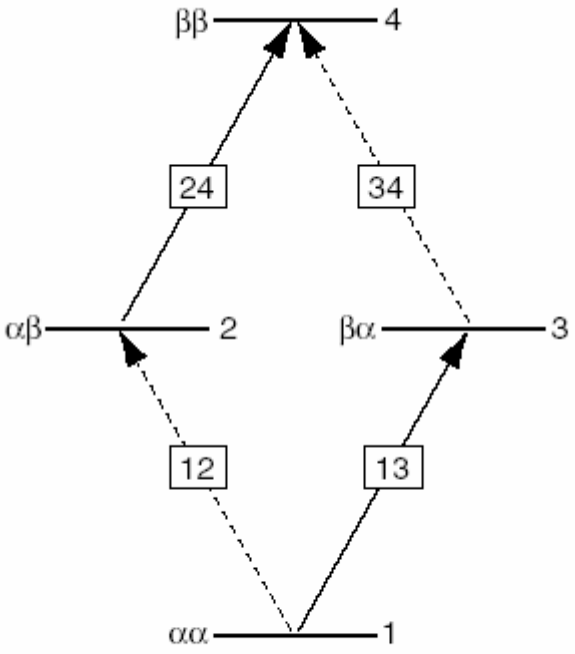
Dva spiny

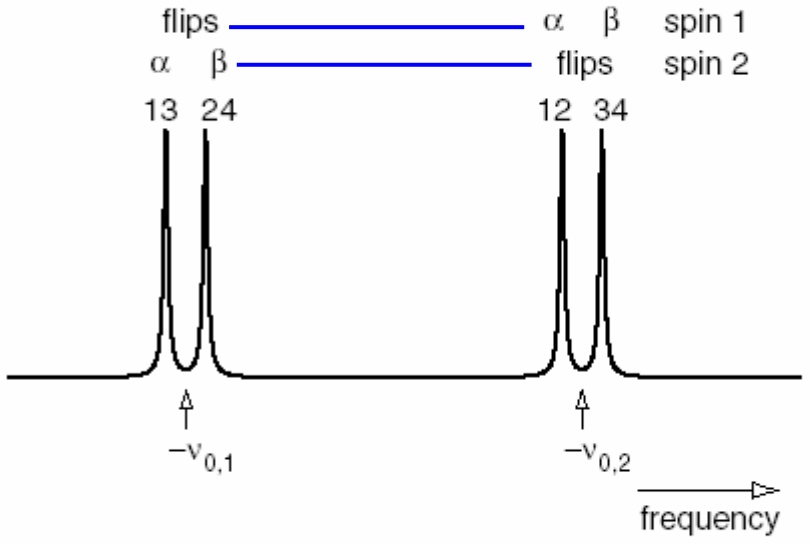
$$\begin{aligned}\nu_{12} &= E_2 - E_1 \\ &= +\tfrac{1}{2}\nu_{0,1} - \tfrac{1}{2}\nu_{0,2} - \tfrac{1}{4}J_{12} - (\tfrac{1}{2}\nu_{0,1} + \tfrac{1}{2}\nu_{0,2} + \tfrac{1}{4}J_{12}) \\ &= -\nu_{0,2} - \tfrac{1}{2}J_{12}.\end{aligned}$$

transition	spin states	frequency
$1 \rightarrow 2$	$\alpha\alpha \rightarrow \alpha\beta$	$-\nu_{0,2} - \frac{1}{2}J_{12}$
$3 \rightarrow 4$	$\beta\alpha \rightarrow \beta\beta$	$-\nu_{0,2} + \frac{1}{2}J_{12}$
$1 \rightarrow 3$	$\alpha\alpha \rightarrow \beta\alpha$	$-\nu_{0,1} - \frac{1}{2}J_{12}$
$2 \rightarrow 4$	$\alpha\beta \rightarrow \beta\beta$	$-\nu_{0,1} + \frac{1}{2}J_{12}$

NMR a energiové hladiny

Dva spiny – jedno-kvantové přechody

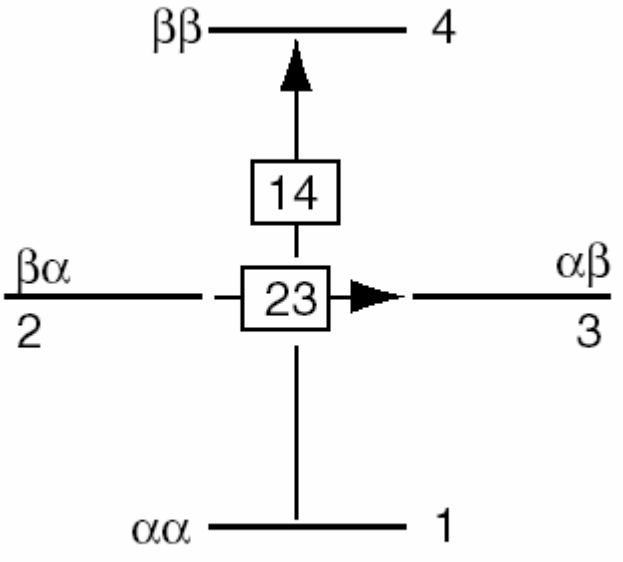




NMR a energiové hladiny

Dva spiny – více-kvantové přechody

number	spin states	M
1	$\alpha\alpha$	1
2	$\alpha\beta$	0
3	$\beta\alpha$	0
4	$\beta\beta$	−1



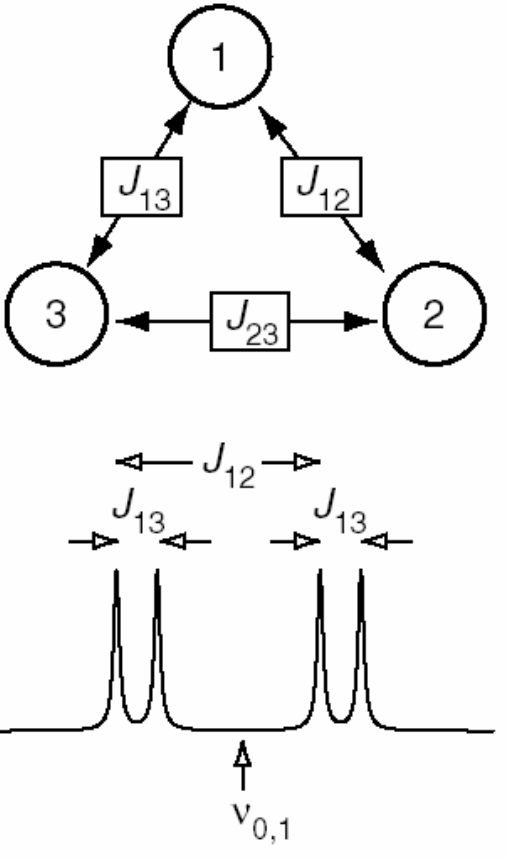
14 – dvou-kvantový přechod
23 – nul-kvantový přechod

NMR a energiové hladiny

Tři spiny

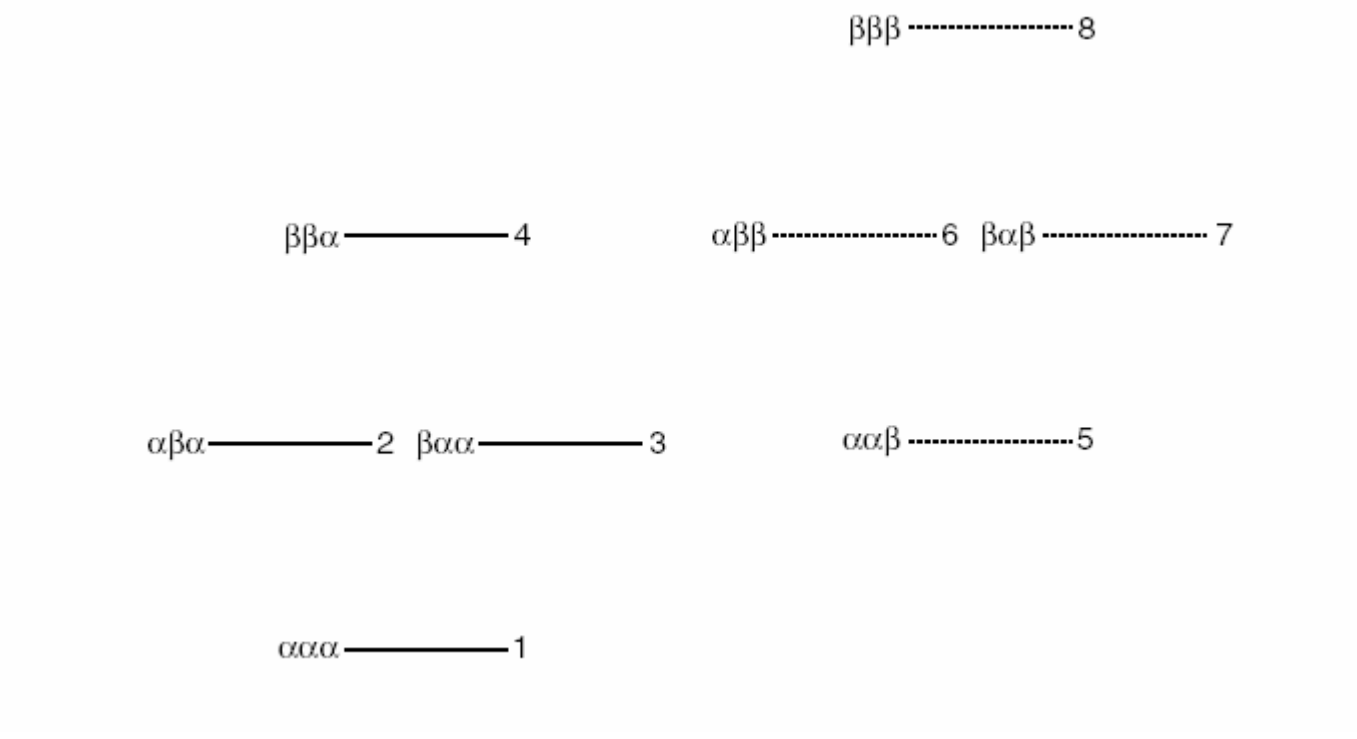
$$E_{m_1 m_2 m_3} = m_1 \nu_{0,1} + m_2 \nu_{0,2} + m_3 \nu_{0,3} + m_1 m_2 J_{12} + m_1 m_3 J_{13} + m_2 m_3 J_{23}$$

number	spin states	M	energy
1	$\alpha\alpha\alpha$	$\frac{3}{2}$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} + \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
2	$\alpha\beta\alpha$	$\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} + \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
3	$\beta\alpha\alpha$	$\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} - \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
4	$\beta\beta\alpha$	$-\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} - \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
5	$\alpha\alpha\beta$	$\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} - \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
6	$\alpha\beta\beta$	$-\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} - \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
7	$\beta\alpha\beta$	$-\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} + \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
8	$\beta\beta\beta$	$-\frac{3}{2}$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} + \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$



NMR a energiové hladiny

Tři spiny



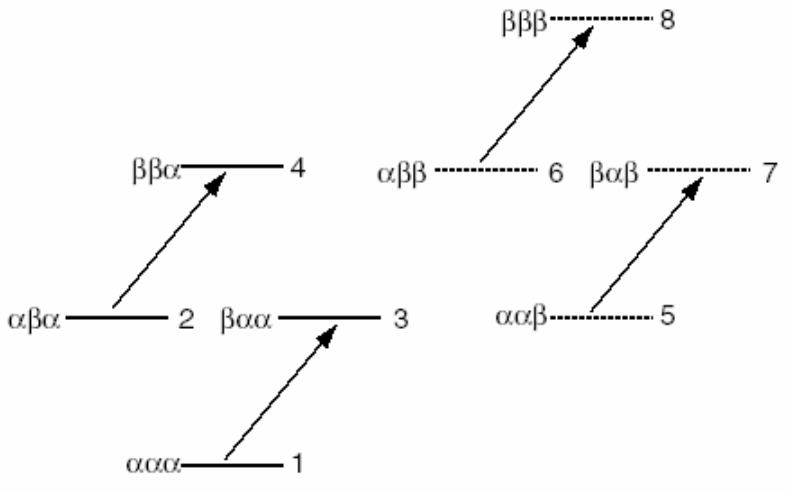
NMR a energiové hladiny

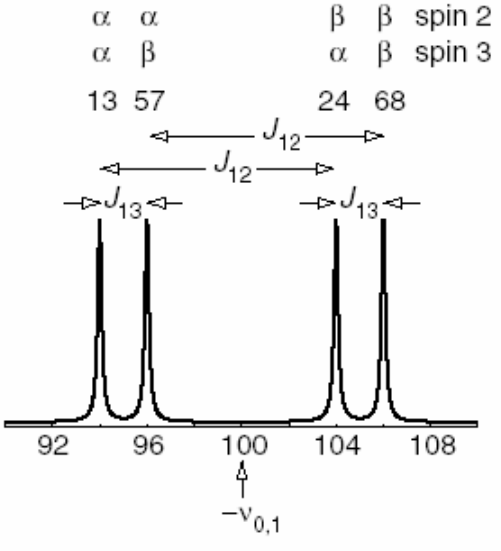
Tři spiny

transition	state of spin 2	state of spin 3	frequency
1–3	α	α	$-\nu_{0,1} - \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
2–4	β	α	$-\nu_{0,1} + \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
5–7	α	β	$-\nu_{0,1} - \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$
6–8	β	β	$-\nu_{0,1} + \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$

Výběrové pravidlo $\Delta M = \pm 1$

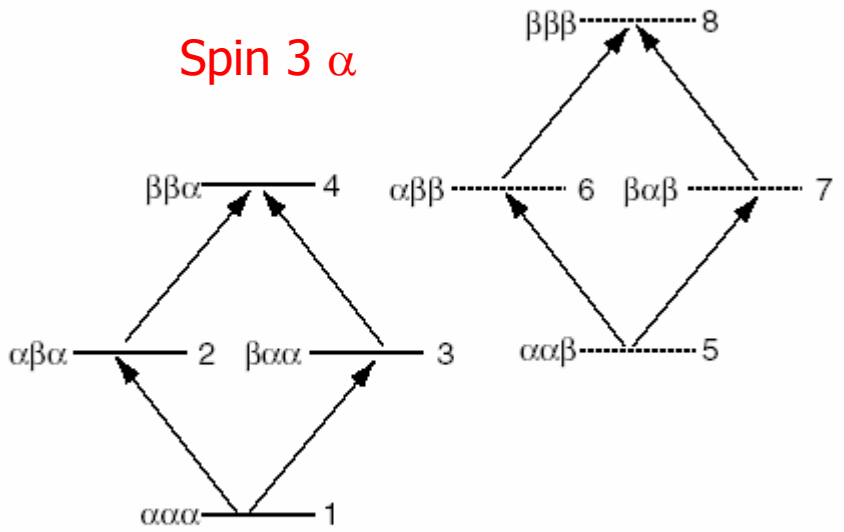
ale jen jeden spin může změnit svůj stav

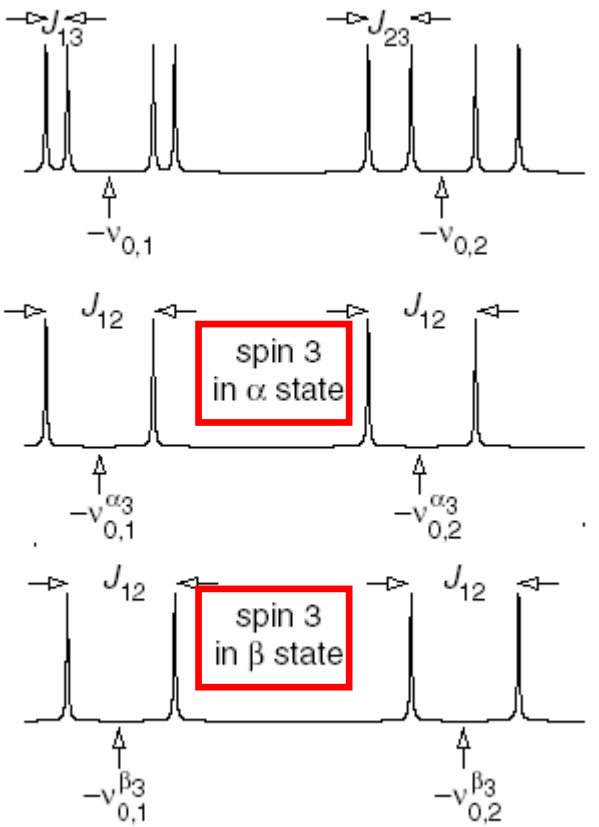




NMR a energiové hladiny

Tři spiny - subspektra





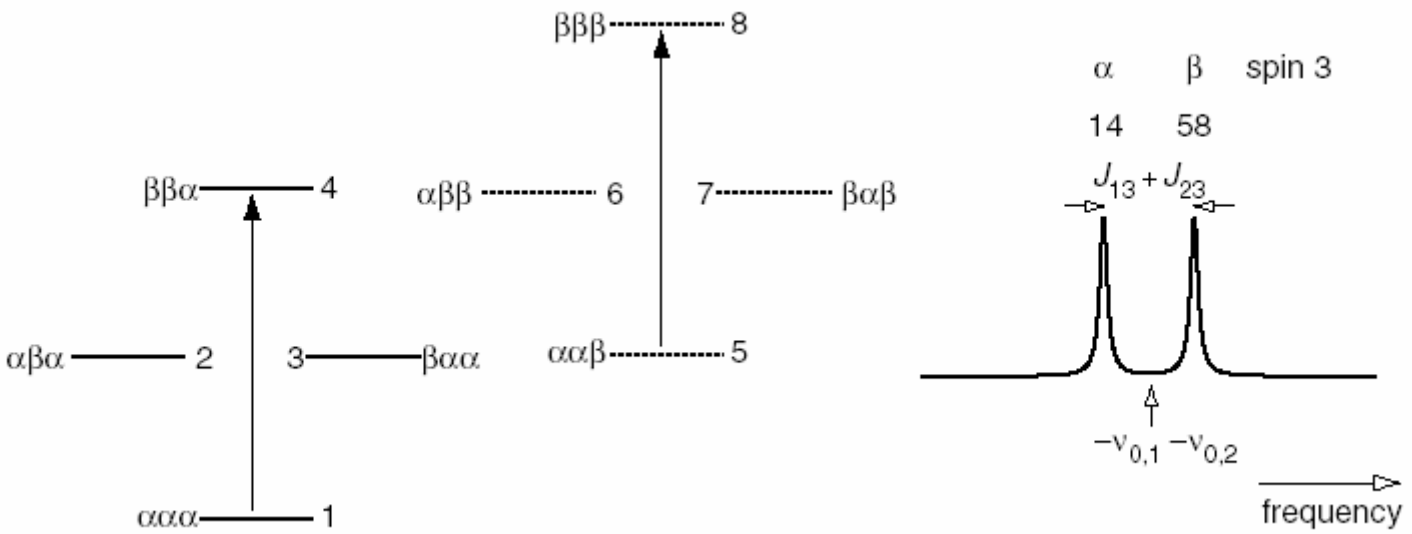
$$\nu_{0,1}^{\alpha_3} = \nu_{0,1} + \tfrac{1}{2}J_{13} \qquad \nu_{0,2}^{\alpha_3} = \nu_{0,2} + \tfrac{1}{2}J_{23}.$$

$$\nu_{0,1}^{\beta_3} = \nu_{0,1} - \tfrac{1}{2}J_{13} \qquad \nu_{0,2}^{\beta_3} = \nu_{0,2} - \tfrac{1}{2}J_{23}.$$

NMR a energiové hladiny

Tři spiny – více-kvantové přechody

transition	initial state	final state	frequency
1–4	$\alpha\alpha\alpha$	$\beta\beta\alpha$	$-\nu_{0,1} - \nu_{0,2} - \frac{1}{2}J_{13} - \frac{1}{2}J_{23}$
5–8	$\alpha\alpha\beta$	$\beta\beta\beta$	$-\nu_{0,1} - \nu_{0,2} + \frac{1}{2}J_{13} + \frac{1}{2}J_{23}$
1–7	$\alpha\alpha\alpha$	$\beta\alpha\beta$	$-\nu_{0,1} - \nu_{0,3} - \frac{1}{2}J_{12} - \frac{1}{2}J_{23}$
2–8	$\alpha\beta\alpha$	$\beta\beta\beta$	$-\nu_{0,1} - \nu_{0,3} + \frac{1}{2}J_{12} + \frac{1}{2}J_{23}$
1–6	$\alpha\alpha\alpha$	$\alpha\beta\beta$	$-\nu_{0,2} - \nu_{0,3} - \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
3–8	$\beta\alpha\alpha$	$\beta\beta\beta$	$-\nu_{0,2} - \nu_{0,3} + \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$



NMR a energiové hladiny

Dva spiny – silná interakce

transition	frequency	intensity
1–2	$\frac{1}{2}D - \frac{1}{2}\Sigma - \frac{1}{2}J_{12}$	$(1 + \sin 2\theta)$
3–4	$\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}$	$(1 - \sin 2\theta)$
1–3	$-\frac{1}{2}D - \frac{1}{2}\Sigma - \frac{1}{2}J_{12}$	$(1 - \sin 2\theta)$
2–4	$-\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}$	$(1 + \sin 2\theta)$

$$\Sigma = \nu_{0,1} + \nu_{0,2} \qquad D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2. \qquad \sin 2\theta = \frac{J_{12}}{D}.$$

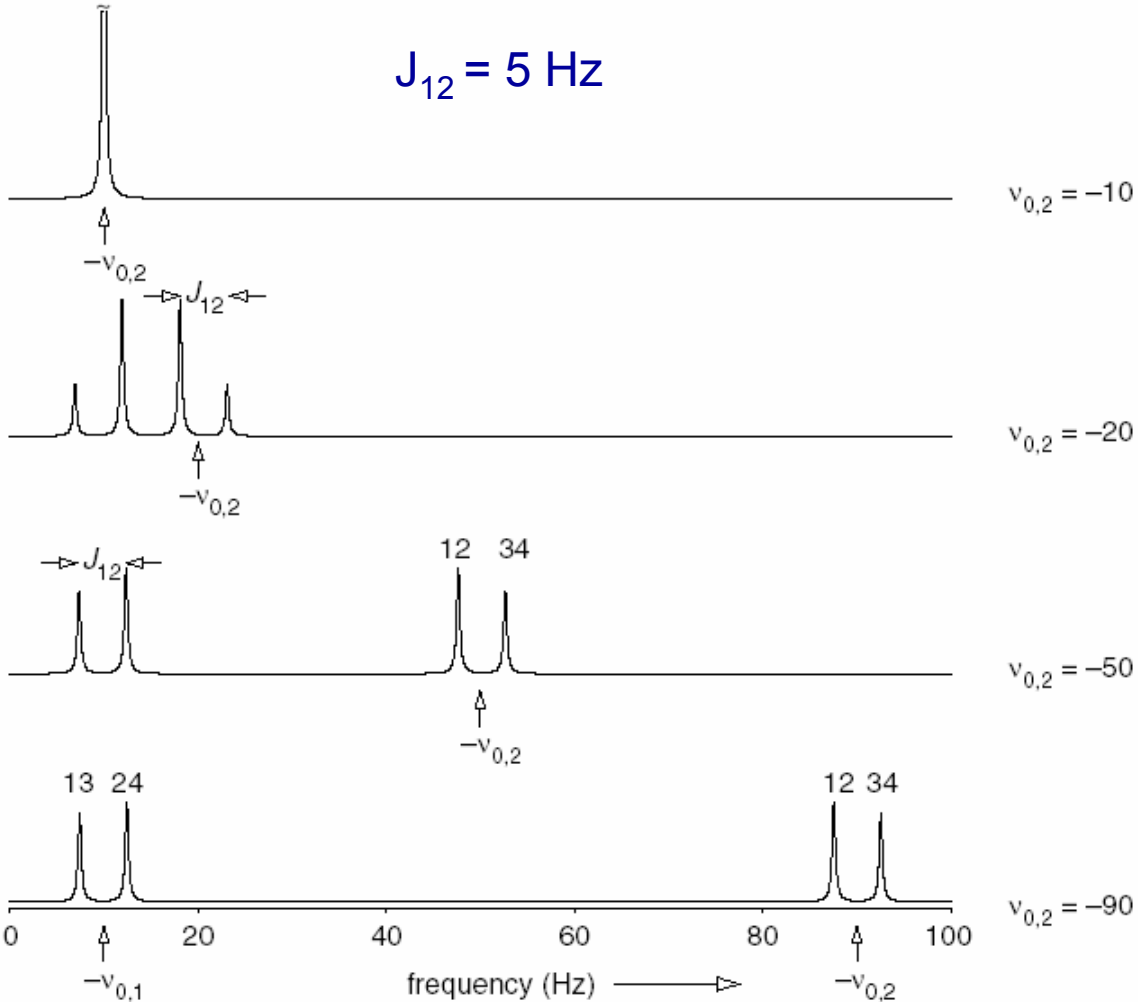
$$\begin{aligned} D^2 &= (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2 \\ &\approx (\nu_{0,1} - \nu_{0,2})^2 \end{aligned}$$

NMR a energiové hladiny

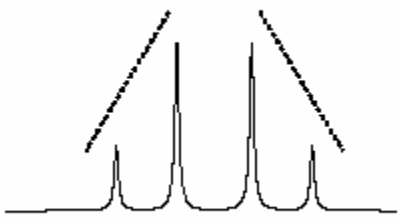
Dva spiny – silná interakce

$\Delta\delta_{12} < 7 * J_{12}$

$J_{12} = 5$ Hz



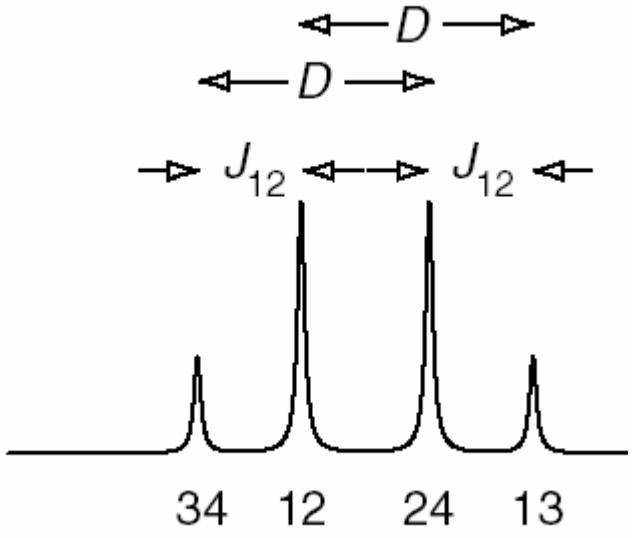
Stříškový efekt



NMR a energiové hladiny

Dva spiny – silná interakce

$\Delta\delta_{12} < 7 * J_{12}$



$$\nu_{34} - \nu_{24} = (\tfrac{1}{2}D - \tfrac{1}{2}\Sigma + \tfrac{1}{2}J_{12}) - (-\tfrac{1}{2}D - \tfrac{1}{2}\Sigma + \tfrac{1}{2}J_{12}) = D.$$

$$D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2$$

$$\nu_{12} + \nu_{24} = (\tfrac{1}{2}D - \tfrac{1}{2}\Sigma - \tfrac{1}{2}J_{12}) + (-\tfrac{1}{2}D - \tfrac{1}{2}\Sigma + \tfrac{1}{2}J_{12}) = -\Sigma.$$

$$\nu_{0,1} = \tfrac{1}{2}(\Sigma + (\nu_{0,1} - \nu_{0,2})) \quad \nu_{0,2} = \tfrac{1}{2}(\Sigma - (\nu_{0,1} - \nu_{0,2}))$$

NMR a energiové hladiny

Tři spiny – ABX systém - subspektra