Magnetska rezonancija

1. Čestice u magnetnom polju

2. Eksperimentalne tehnike

3. NMR spektroskopija

Čestice u magnetskom polju

Čestice koje posjeduju spinsku kutnu količnu gibanja orijentiraju se u magnetskom polju.

Elektron e, e^-

Kvantni broj elektronskog spina *s*

$$s = \frac{1}{2}$$

$$\left| \boldsymbol{S} \right| = \sqrt{s(s+1)}\ \hbar = \sqrt{3/4}\ \hbar$$

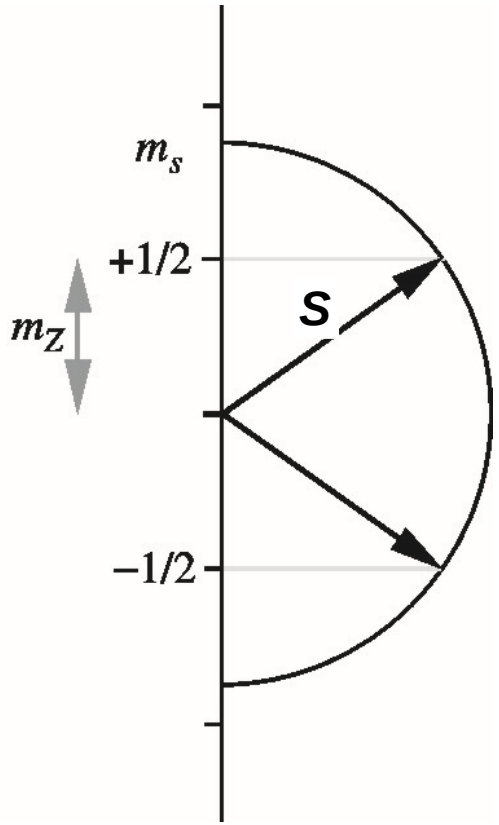
z-komponenta elektronskog spina

magnetski kvantni broj spina

m_s

$$m_s \rightarrow +\frac{1}{2}, -\frac{1}{2}$$

$$S_Z = m_s \hbar = \pm \tfrac{1}{2} \hbar$$



Proton p, p^+, $^1H^+$

$$|\boldsymbol{I}| = \sqrt{I(I+1)}\,\hbar = \sqrt{3/4}\,\hbar$$

$$I_Z = m_I\,\hbar = \pm\tfrac{1}{2}\,\hbar$$

Jezgre

$$|\boldsymbol{I}| = \sqrt{I(I+1)}\,\hbar \qquad\qquad I_Z = m_I\,\hbar$$

Kvantni broj nuklearnog spina I

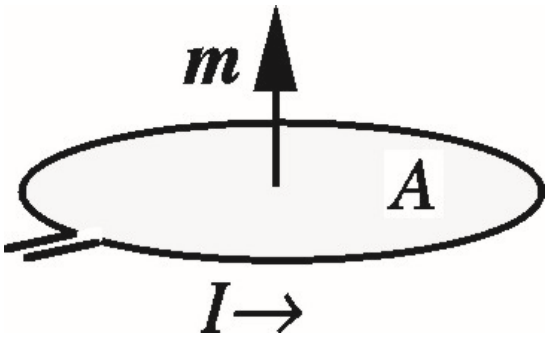
$$I \rightarrow 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$$

Z-komponenta nuklearnog spina
magnetski kvantni broj nukelarnog spina m_I

$$m_I \rightarrow I, I-1, \ldots, 0, \ldots -I+1, -I$$

$$m_I \rightarrow I, I-1, \ldots, \frac{1}{2}, -\frac{1}{2}, \ldots -I$$

Magnetski moment strujne petlje

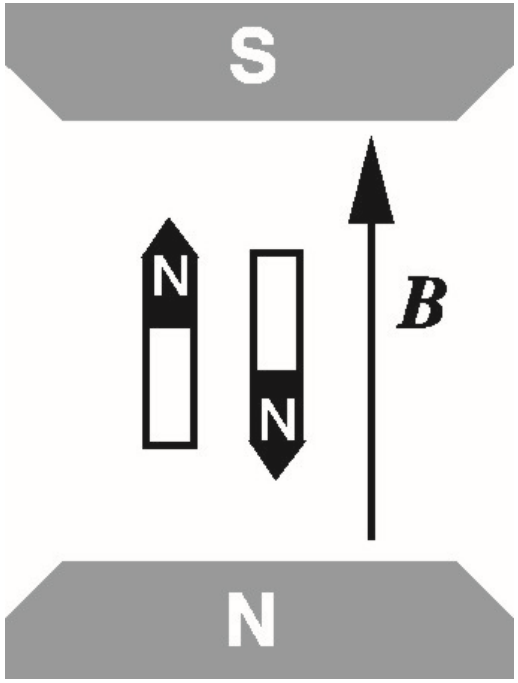


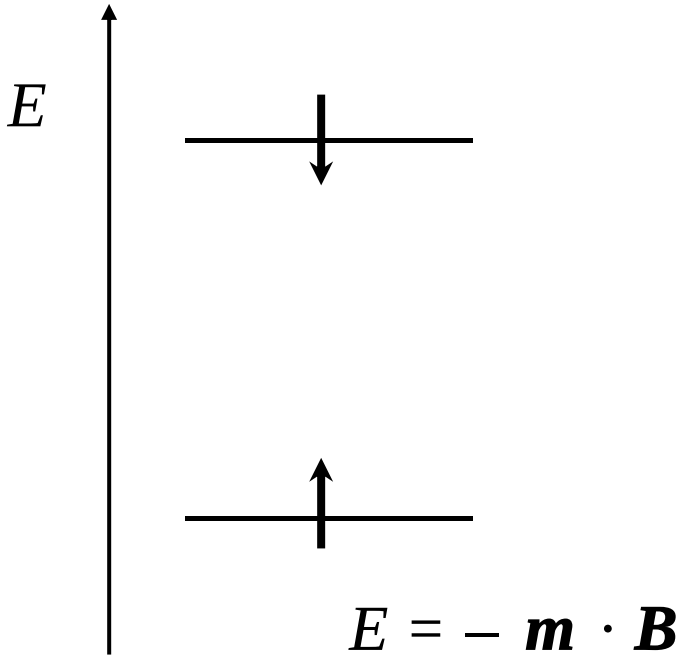
$$\boldsymbol{m} = I\,\boldsymbol{A}$$

$$|\boldsymbol{m}| = \frac{Qv}{2r\pi} r^2\pi = \frac{Qvr}{2}$$

$$L = mvr$$

$$\gamma = \frac{|\boldsymbol{m}|}{|\boldsymbol{L}|} = \frac{|Q|}{2m} \quad = \left(\frac{g\,e}{2m}\right)$$





$$E = - \boldsymbol{m} \cdot \boldsymbol{B}$$

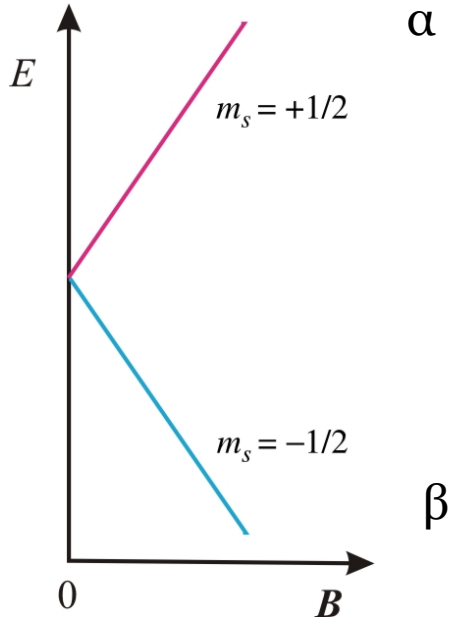
Elektron

Magnetski moment elektrona

$$\boldsymbol{m} = g\,\frac{-e\hbar}{2m_{\mathrm{e}}}\sqrt{s(s+1)}$$

$$\boldsymbol{m} = -g\;\mu_{\mathrm{B}}\;\sqrt{s(s+1)}$$

Bohrov magneton $\mu_{\mathrm{B}} = \dfrac{e\hbar}{2m_{\mathrm{e}}} \approx 9{,}273\times10^{-24}\ \mathrm{J\ T^{-1}}$



Komponenta magnetskog momenta elektrona duž osi Z

$$m_{\mathrm{Z}} = -g\;\mu_{\mathrm{B}}\;m_s$$

Energija interakcije magnetskog momenta *m* s magnetskom indukcijom *B*

$$E = -\,\boldsymbol{m}\cdot\boldsymbol{B}$$

$$E = g\;\mu_{\mathrm{B}}\;m_s B$$

Jezgra

Magnetski moment jezgre

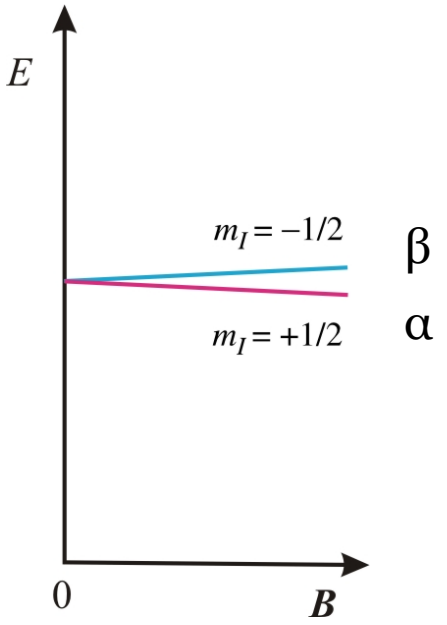
$$\boldsymbol{m} = g\,\frac{e\hbar}{2m_{\mathrm{p}}}\sqrt{I(I+1)}$$

$$\boldsymbol{m} = g\;\mu_{\mathrm{N}}\;\sqrt{I(I+1)}$$

Nuklearni magneton $\mu_{\mathrm{N}} = \dfrac{e\hbar}{2m_{\mathrm{p}}} \approx 5{,}051\times10^{-27}\ \mathrm{J\ T^{-1}}$

Komponenta magnetskog momenta jezgre duž osi Z

$$m_Z = g\;\mu_{\mathrm{N}}\;m_I$$

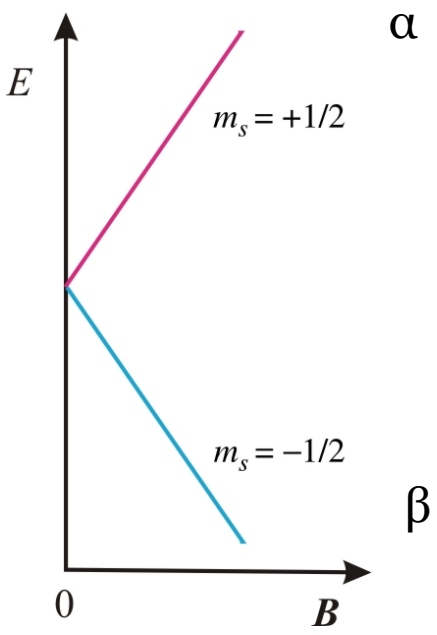


Energija interakcije magnetskog momenta *m* s magnetskom indukcijom *B (jezgra s I = ½)*

$$E = -\,\boldsymbol{m}\cdot\boldsymbol{B}$$

$$E = -g\;\mu_{\mathrm{N}}\;m_I B$$

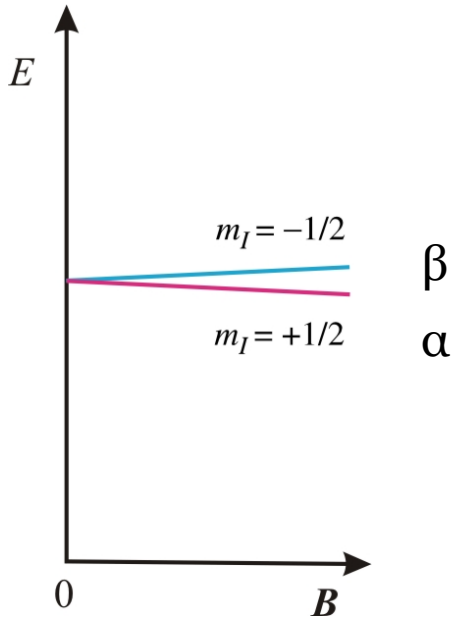
Elektron



$$E = -g\ \mu_{\mathrm{B}}\ m_I B$$

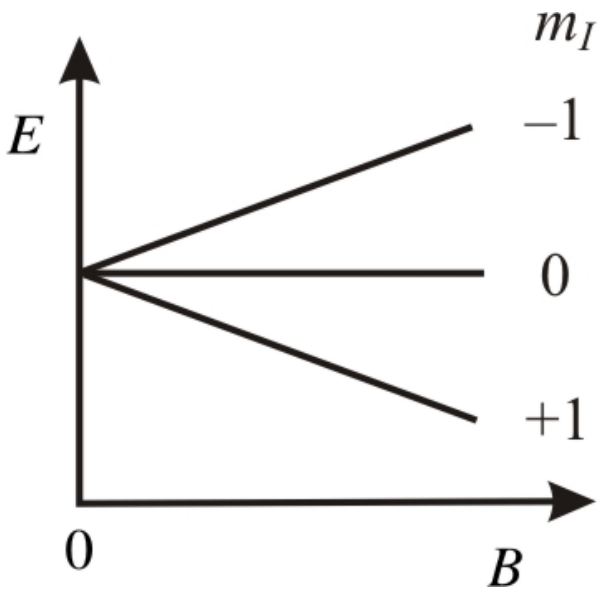
$$\frac{\mu_{\mathrm{B}}}{\mu_{\mathrm{N}}} = \frac{m_{\mathrm{p}}}{m_{\mathrm{e}}}$$

Jezgra ($m_I = \pm\frac{1}{2}$)

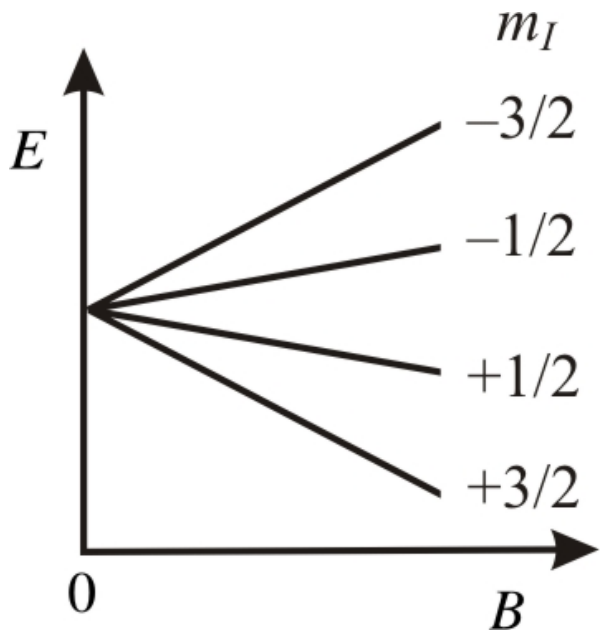


$$E = -g\ \mu_{\mathrm{N}}\ m_I B$$

$I = 1$



$I = 3/2$



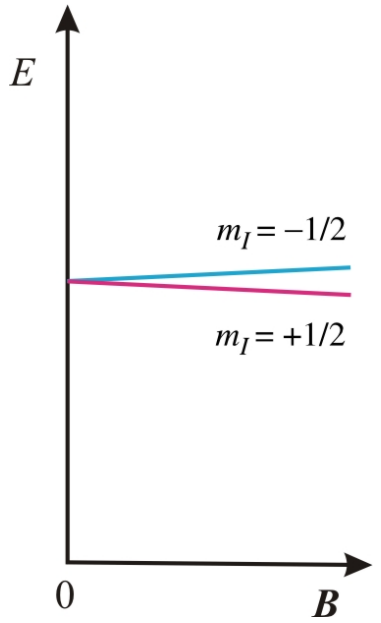
$$E = -g\ \mu_{\mathrm{N}}\ m_I B$$

Frekvencija rezonancije

Jezgra ($m_I = \pm\frac{1}{2}$)

$$\nu = \frac{\Delta E}{h}$$

$$\Delta m_I = \pm 1$$



$$\Delta E = E(m_I - 1) - E(m_I) = g\mu_N B = h\nu_L$$

Popunjenost energetskih razina

- Boltzmanova raspodjela

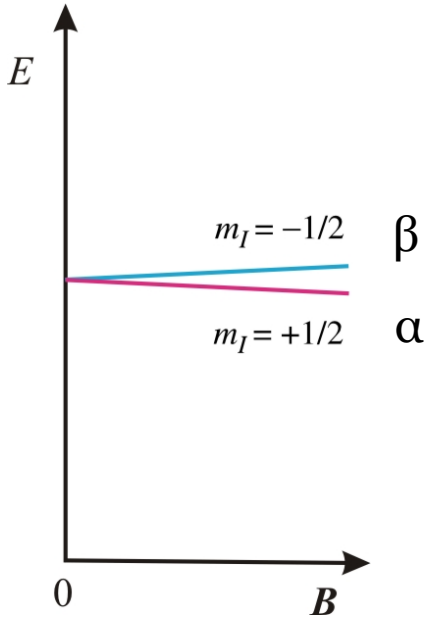
$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\left(E_\beta - E_\alpha\right)}{k_B T}\right)$$

$$E_\beta - E_\alpha > 0$$

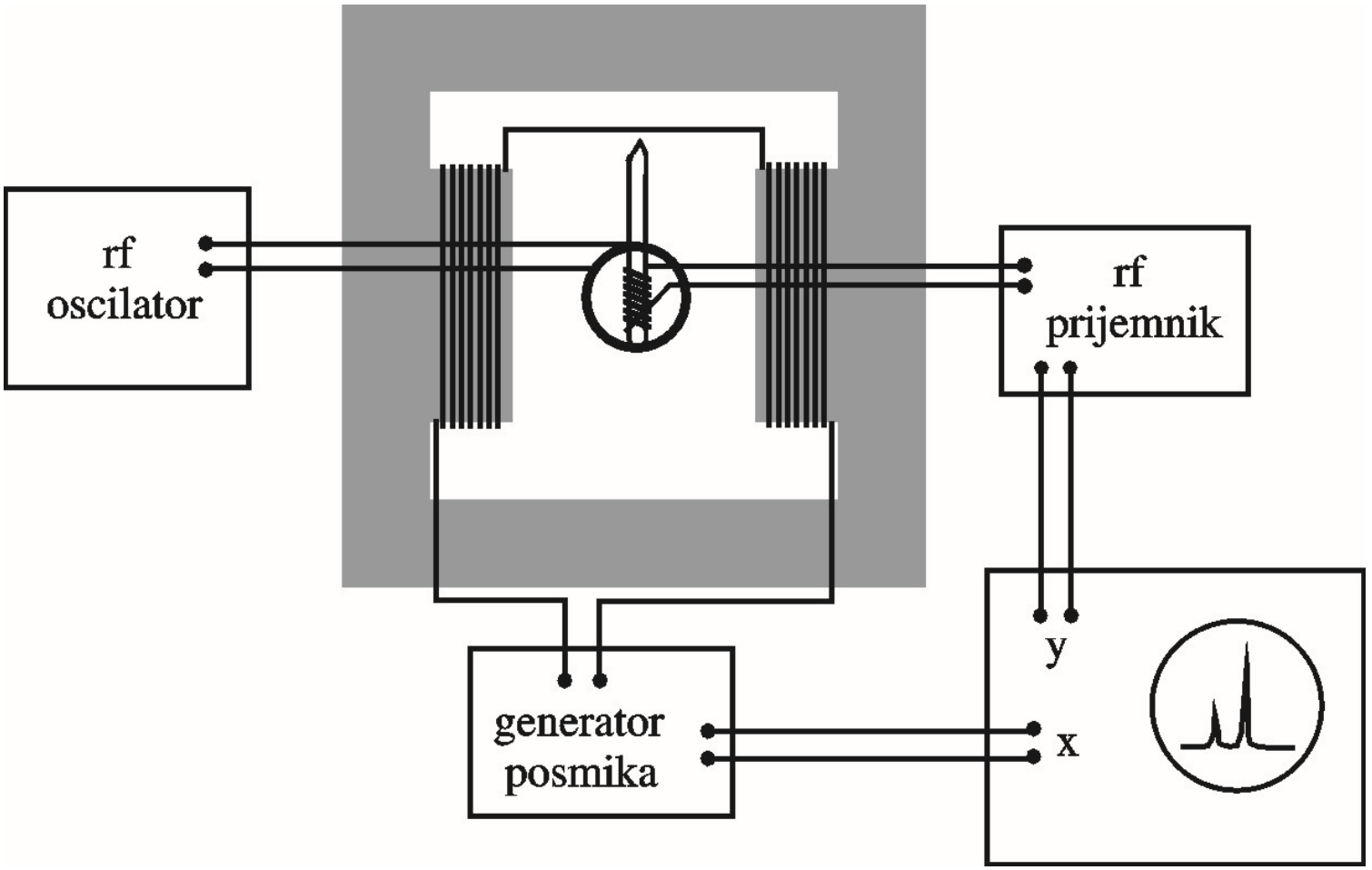
$$\frac{N_\beta}{N_\alpha} < 1$$

$$N_\beta < N_\alpha$$

Jezgra ($m_I = \pm\frac{1}{2}$)

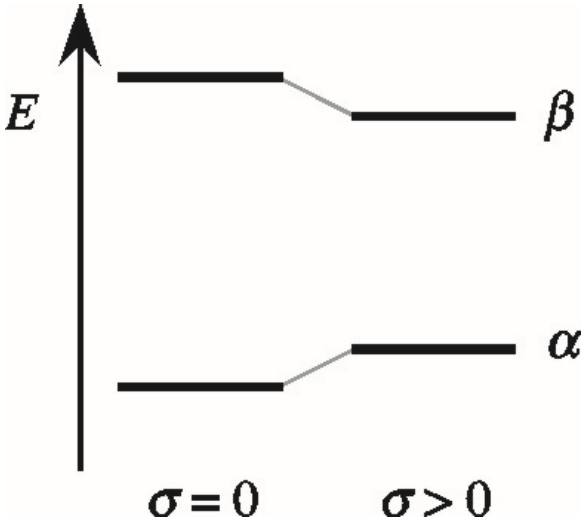


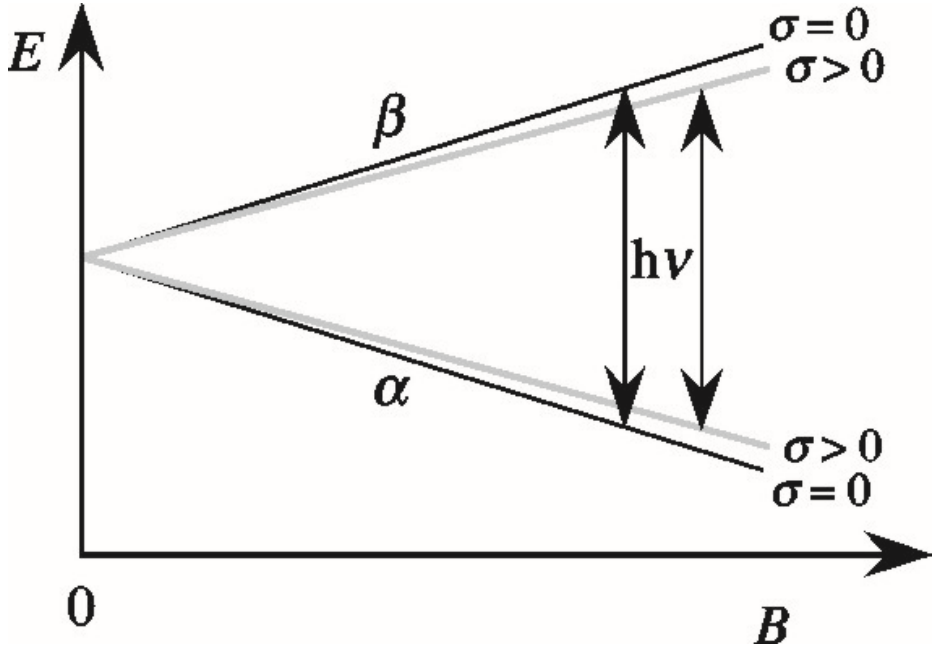
Shema NMR spektrometra



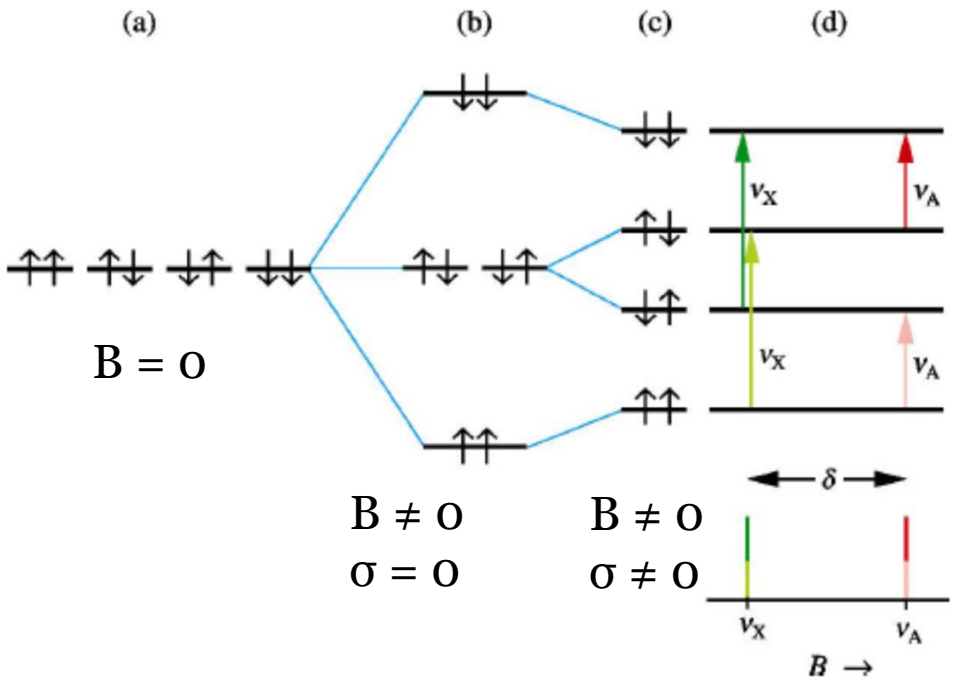
Kemijski pomak

$$B = B_0(1-\sigma)$$





1) RAZINE SPINSKIH STANJA DVAJU PROTONA



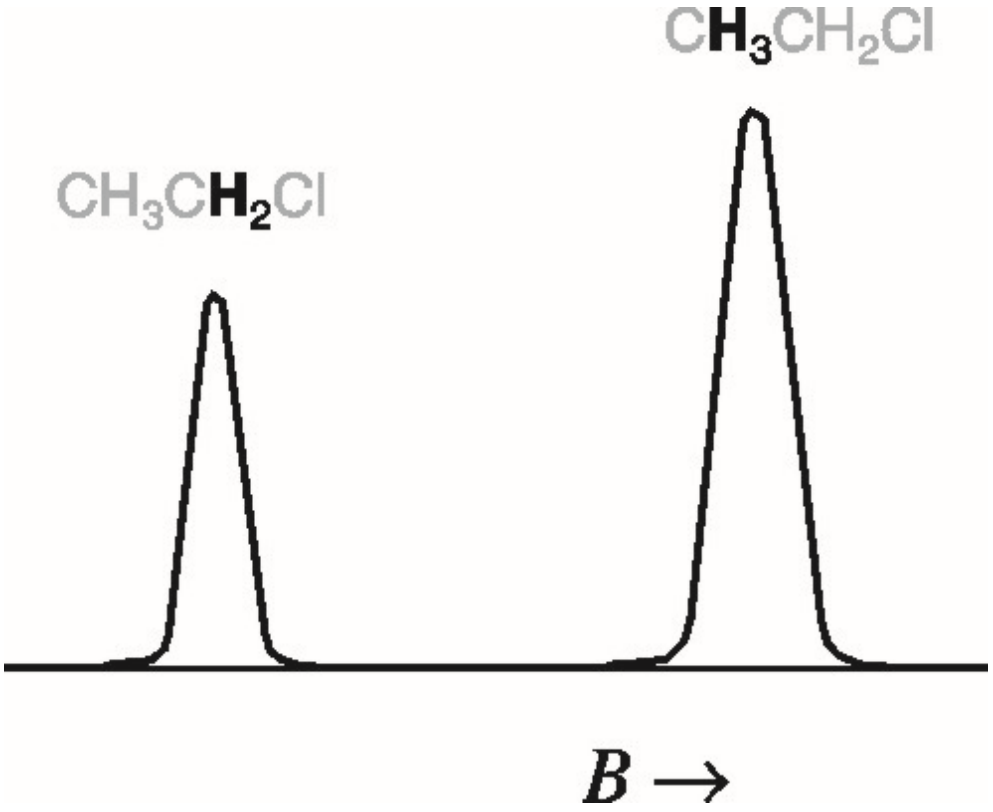
PRIJELAZI

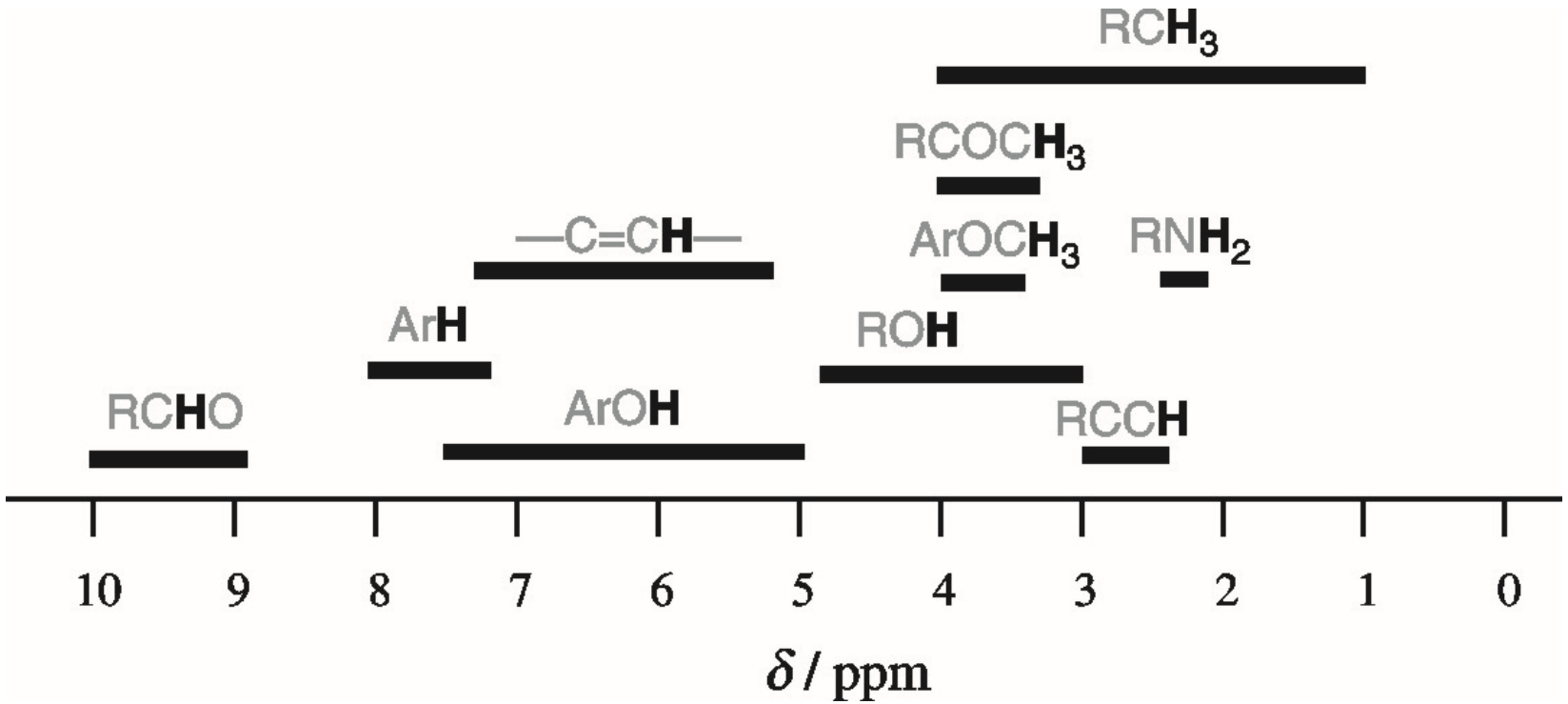
SPEKTAR

$$\delta_X = \left(\sigma_{ref} - \sigma_X\right) \times 10^6 \text{ ppm}$$

$$\delta_X \approx \frac{B_i - B_{ref}}{B_{ref}} \times 10^6 \text{ ppm} = \frac{B_0(1-\sigma_X) - B_0(1-\sigma_{ref})}{B_0(1-\sigma_{ref})} \times 10^6 \text{ ppm}$$

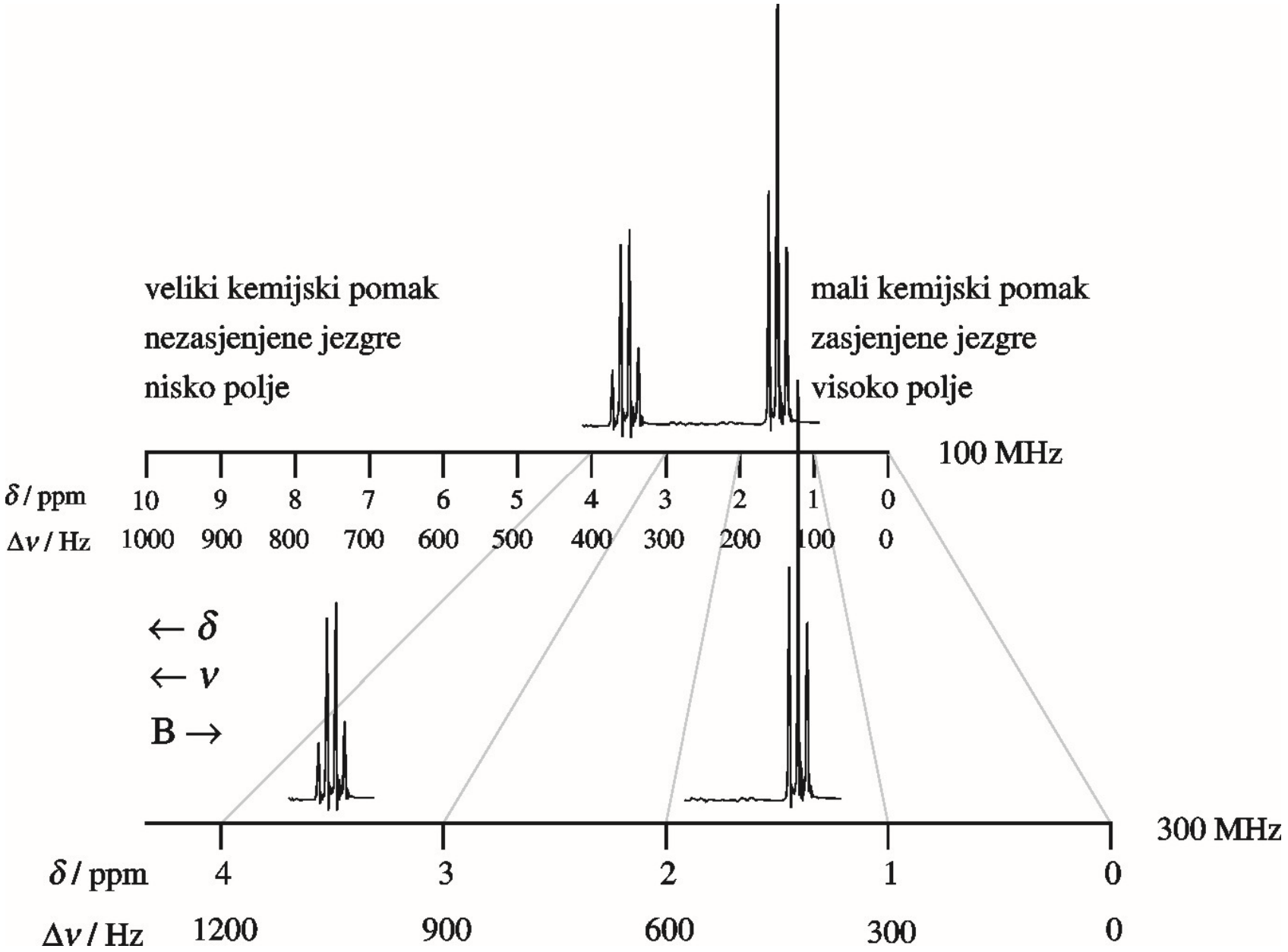
$$\delta_X \approx \frac{\Delta\nu}{\nu_{ref}} \times 10^6 \text{ ppm}$$





Zasjenjenje:

- lokalni doprinos (elektroni)
- doprinosi susjednih i daljnih atoma
- doprinos otapala


veliki kemijski pomak
nezasjenjene jezgre
nisko polje
mali kemijski pomak
zasjenjene jezgre
visoko polje
100 MHz
δ / ppm 10 9 8 7 6 5 4 3 2 1 0
Δν / Hz 1000 900 800 700 600 500 400 300 200 100 0
← δ
← ν
B →
300 MHz
δ / ppm 4 3 2 1 0
Δν / Hz 1200 900 600 300 0

Cijepanje signala

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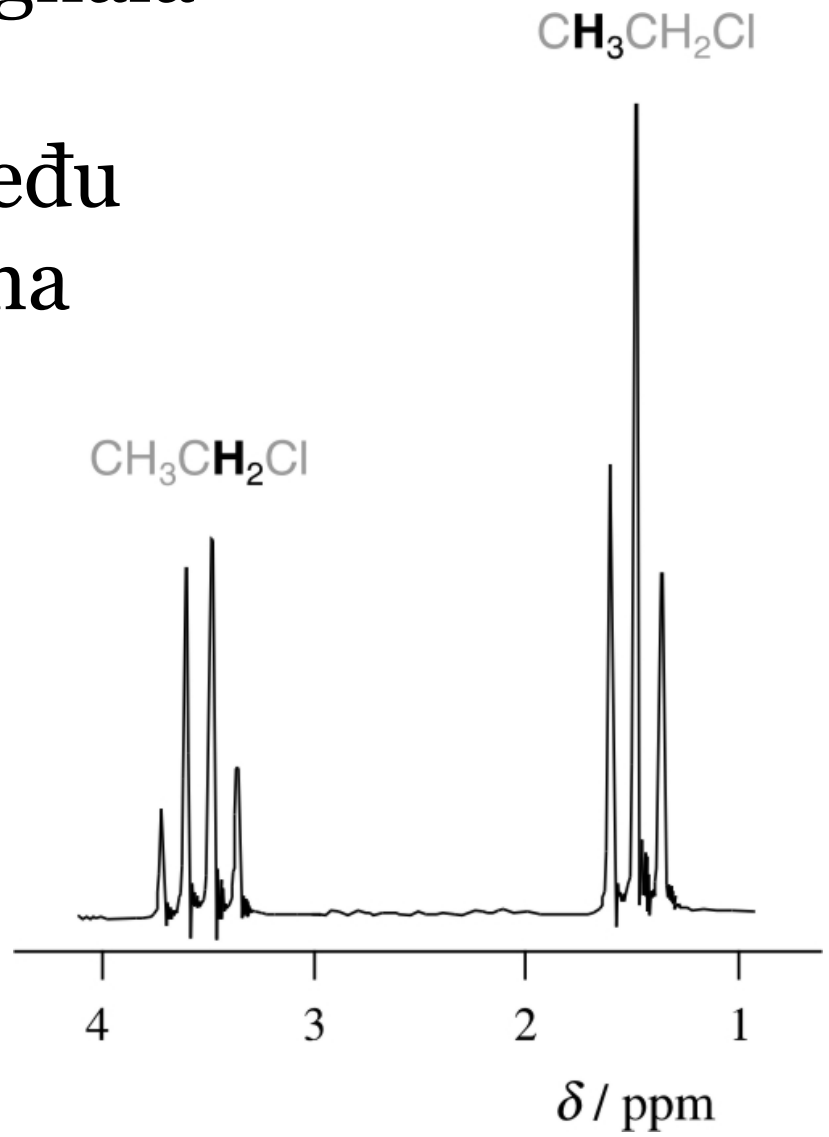
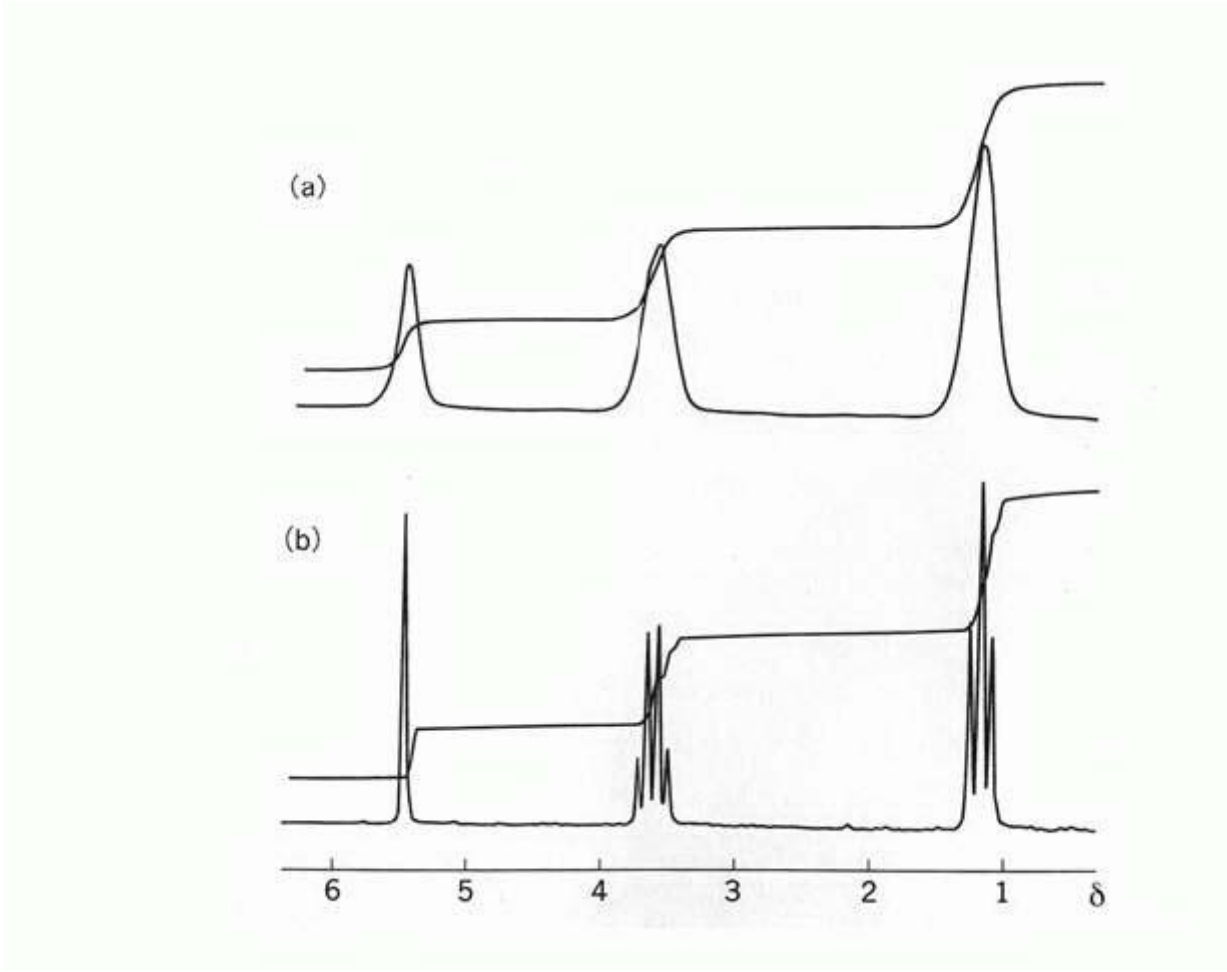
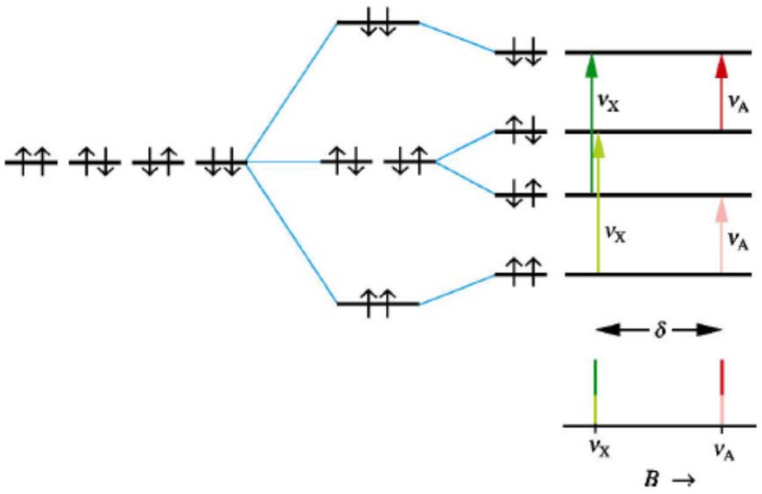
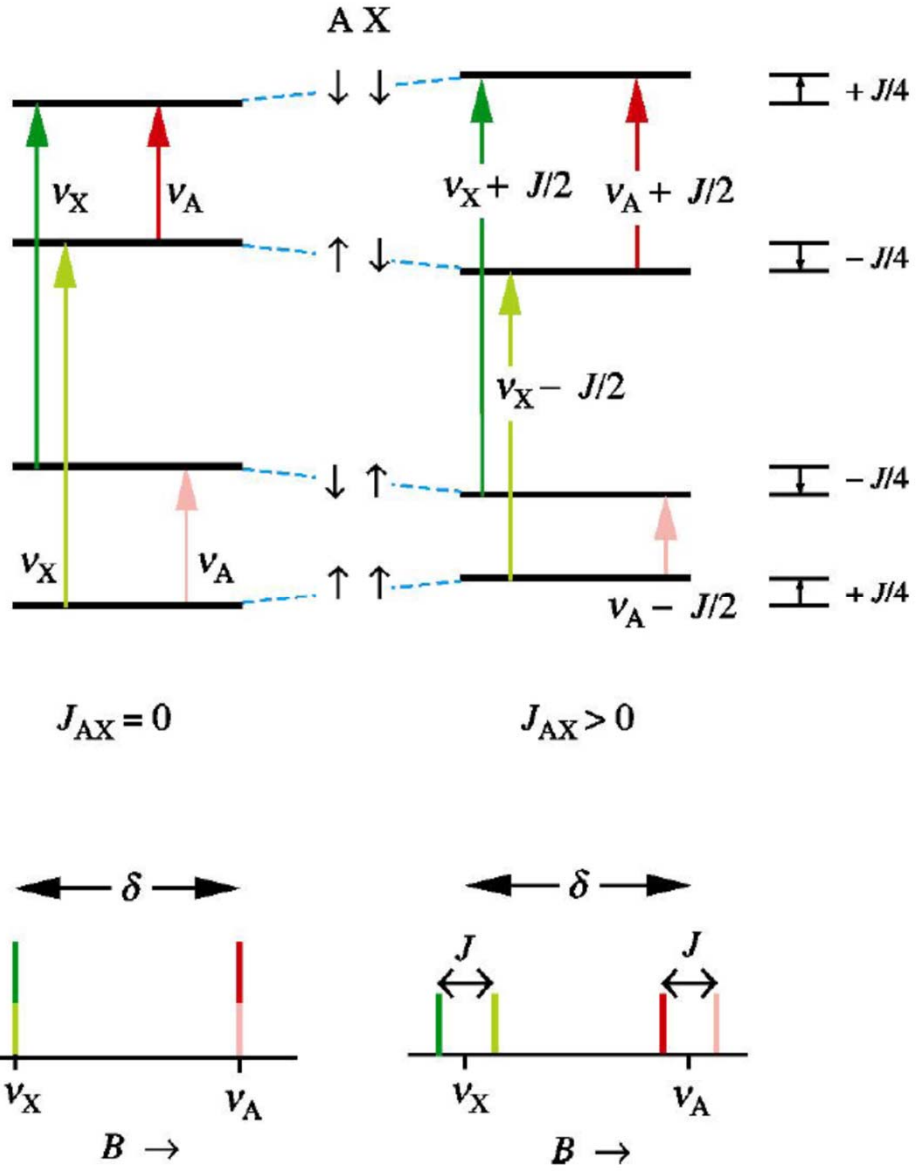
Sprega među spinovima





CH_3CH_2OH

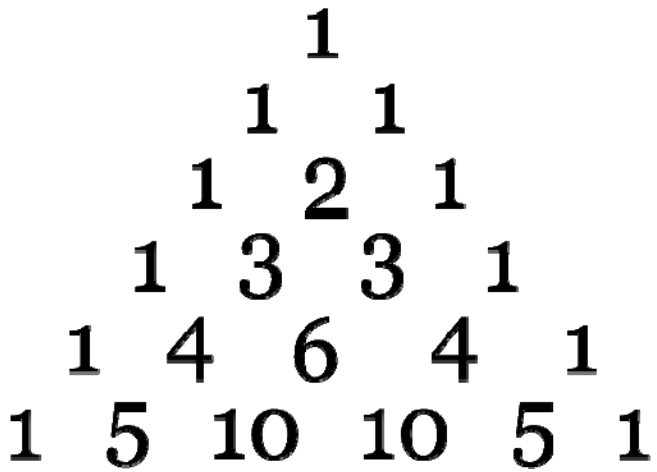

ν_X
ν_A
ν_X
ν_A
δ
ν_X
ν_A
$B \rightarrow$

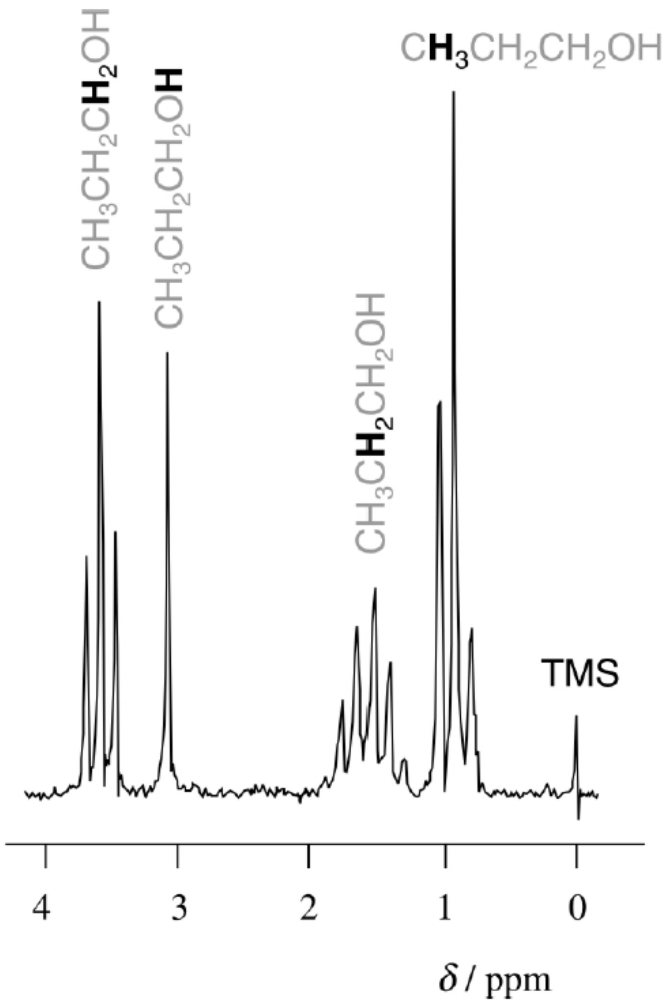

A X
$+ J/4$
ν_X
ν_A
$\nu_X + J/2$
$\nu_A + J/2$
$- J/4$
$\nu_X - J/2$
$- J/4$
ν_X
ν_A
$+ J/4$
$\nu_A - J/2$
$J_{AX} = 0$
$J_{AX} > 0$
δ
ν_X
ν_A
$B \rightarrow$
δ
J
J
ν_X
ν_A
$B \rightarrow$

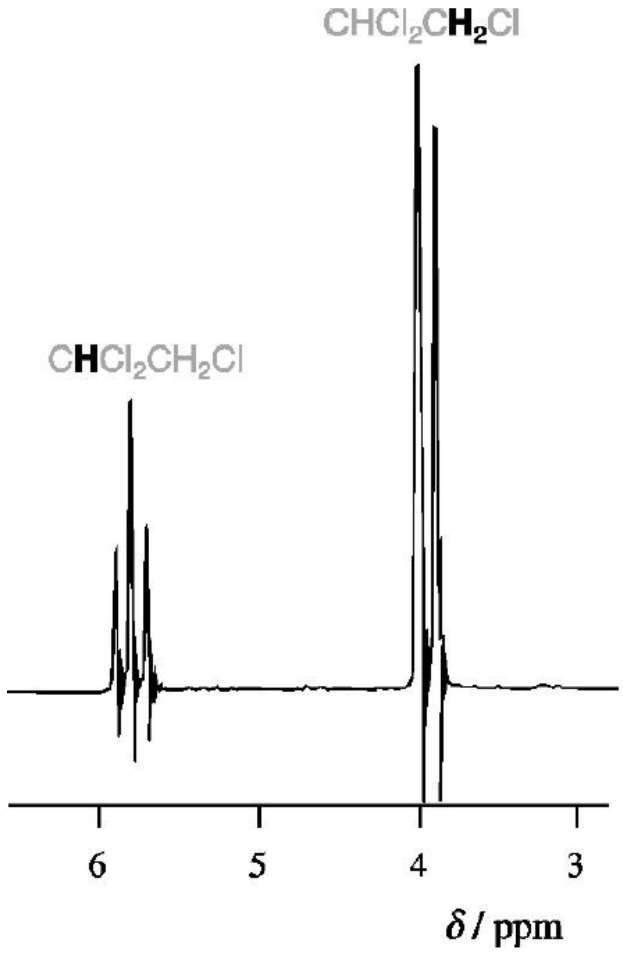
Cijepanje linija
- spin-spin sprega

N susjednih protona → N+1 LINIJA

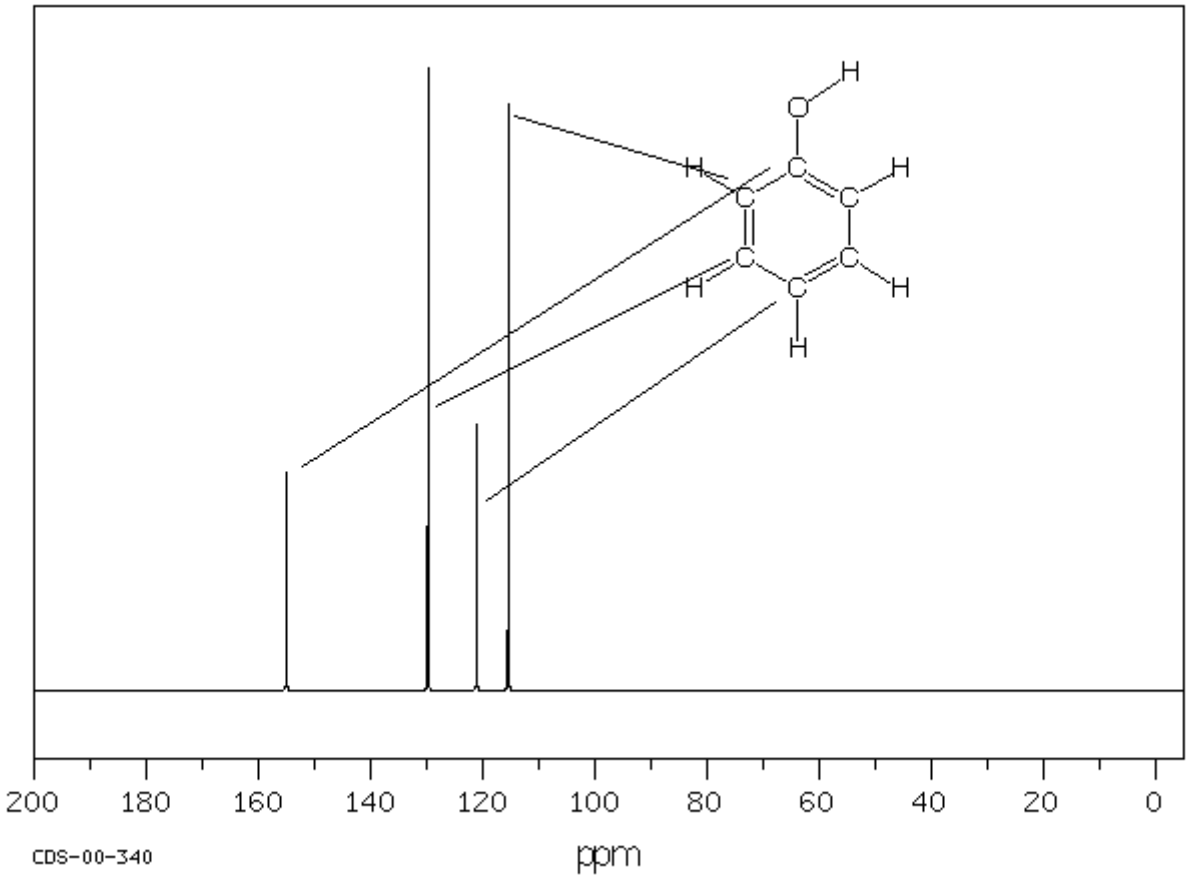
Intenziteti: Pascalov trokut




CH3CH2CH2OH
CH3CH2CH2OH
CH3CH2CH2OH
CH3CH2CH2OH
TMS
4
3
2
1
0
δ / ppm


CHCl2CH2Cl
CHCl2CH2Cl
6
5
4
3
δ / ppm

^{13}C - NMR


H
O
H
C
H
C
C
C
C
H
H
C
H
H
200
180
160
140
120
100
80
60
40
20
0
CDS-00-340
ppm

MAGNETSKA REZONANCIJA

1. Koje jezgre imaju magnetski moment?
2. Koliko je mogućih orijentacija magnetskog momenta ako je nuklearni spinski kvantni broj 9/2 (^{209}Bi)?
3. Koliko je mogućih orijentacija magnetskog momenta ako je nuklearni spinski kvantni broj 8 (^{180}Ta)?
4. Nabrojite neke jezgre s $I = 0$.
5. Nabrojite neke jezgre s $I = 1/2$.
6. Koja je čestica jači magnet: elektron ili proton?
7. Kakva je energija interakcije magnetskog momenta s magnetskim poljem?
8. Što je Larmorova frekvencija?
9. Kako ovisi separacija energijskih razina o magnetskoj indukciji primjenjenog magneta?
10. Što inducira prijelaze među nuklearnim spinskim razinama?
11. Koje se zračenje primjenjuje u NMR?

NMR

1. Kojeg su reda veličine magnetske indukcije kod NMR-spektrometara?
2. Što je uzrok kemijskom pomaku?
3. Što iskazuje konstanta zasjenjenja?
4. Zašto elektroni slabe utjecaj vanjskog polja na jezgre?
5. Kakav efekt na spektar ima zasjenjenje jezgara?
7. Zašto su kemijski pomaci kod ugljika znatno veći nego kod protona?
8. Prikažite energijske razine i prijelaze za dva protona u različitim kemijskim sredinama.
9. Koji utjecaji pridonose kemijskom pomaku?
10. Kako susjedni atomi utječu na kemijski pomak?

Objasnite sprezanja među spinovima vodikovih atoma susjednih funkcionalnih skupina?

12. Objasnite nastajanje tripleta linija.
13. Objasnite nastajanje kvadrupleta linija.