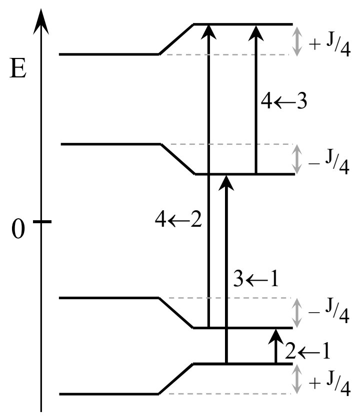
Spin-Spin Splitting in NMR

if $\nu_A - \nu_B >> J_{AB}$ $\qquad \hat{\mathcal{H}}/h \cong -\nu_A \hat{I}_{zA} - \nu_B \hat{I}_{zB} + J_{AB}\hat{I}_{zA}\hat{I}_{zB}$

$\hat{I}_z \alpha = \frac{1}{2}\alpha \qquad \hat{I}_z \beta = \frac{1}{2}\beta \qquad$ with $m_z = \pm\frac{1}{2}$ for A or B

m_{zA}	m_{zB}	AB	no coupling with coupling	$E = -\nu_A m_{zA} - \nu_B m_{zB} + J_{AB}$
–½	–½	ββ		$+\frac{\nu_A}{2} \quad +\frac{\nu_B}{2} \quad +\frac{J_{AB}}{4}$
–½	+½	βα		$+\frac{\nu_A}{2} \quad -\frac{\nu_B}{2} \quad -\frac{J_{AB}}{4}$
+½	–½	αβ		$-\frac{\nu_A}{2} \quad +\frac{\nu_B}{2} \quad -\frac{J_{AB}}{4}$
+½	+½	αα		$-\frac{\nu_A}{2} \quad -\frac{\nu_B}{2} \quad +\frac{J_{AB}}{4}$



Transitions:

$$4\leftarrow 2:\ \Delta E = \left(+\frac{\nu_A}{2}+\frac{\nu_B}{2}+\frac{J_{AB}}{4}\right)-\left(-\frac{\nu_A}{2}+\frac{\nu_B}{2}-\frac{J_{AB}}{4}\right)=\nu_A+\frac{J_{AB}}{2}$$

$$3\leftarrow 1:\ \Delta E = \left(+\frac{\nu_A}{2}-\frac{\nu_B}{2}-\frac{J_{AB}}{4}\right)-\left(-\frac{\nu_A}{2}-\frac{\nu_B}{2}+\frac{J_{AB}}{4}\right)=\nu_A-\frac{J_{AB}}{2}$$

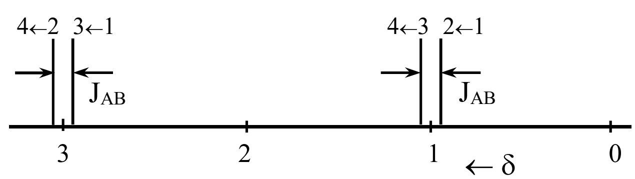
$$4\leftarrow 3:\ \Delta E = \left(+\frac{\nu_A}{2}+\frac{\nu_B}{2}+\frac{J_{AB}}{4}\right)-\left(+\frac{\nu_A}{2}-\frac{\nu_B}{2}-\frac{J_{AB}}{4}\right)=\nu_B+\frac{J_{AB}}{2}$$

$$2\leftarrow 1:\ \Delta E = \left(-\frac{\nu_A}{2}+\frac{\nu_B}{2}-\frac{J_{AB}}{4}\right)-\left(-\frac{\nu_A}{2}-\frac{\nu_B}{2}+\frac{J_{AB}}{4}\right)=\nu_B-\frac{J_{AB}}{2}$$

Example: let ν_A = 3 ppm, ν_B = 1 ppm, and J_{AB} = 0.03 ppm (i.e. 9 Hz at 300 MHz)

4←2: ΔE = 3 + 0.03/2 $\quad$ 3←1: ΔE = 3 – 0.03/2

4←3: ΔE = 1 + 0.03/2 $\quad$ 2←1: ΔE = 1 – 0.03/2

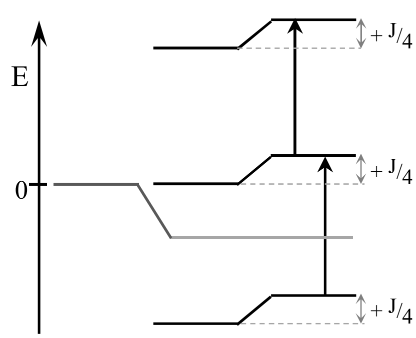


$\nu_A = \nu_B$ $\qquad \hat{\mathcal{H}}/h = -\nu_A \hat{I}_{zA} - \nu_B \hat{I}_{zB} + J_{AB}\vec{I}_A\cdot\vec{I}_B$

ββ

$^1/\sqrt{2}\,(\alpha\beta - \beta\alpha)$, $^1/\sqrt{2}\,(\alpha\beta + \beta\alpha)$

αα



equivalent protons don't split